TECHNICAL REPORT
68-33-CM

SYNTHESIS OF NEW FLUORINE-CONTAINING NITROSO COMPOUNDS, COPOLYMERS AND TERPOLYMERS

by

Eugene C. Stump and Calvin D. Padgett
Peninsular Chem Research, Inc.
Gainesville, Florida

Contract No. DA19-129-AMC-152 (N)

November 1967

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing and Organic Materials Laboratory
C&OM-38

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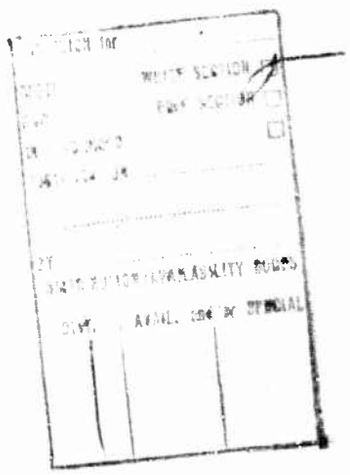

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FOREWORD

This is a final report covering research conducted by Peninsular ChemResearch, Inc., Gainesville, Florida from July 1, 1963 to November 26, 1966. The purpose of this project was to investigate the modification of nitroso rubber by incorporation of various other atoms and groups to give either enhanced physical properties or to provide reactive sites for cross-linking. As a necessary adjunct to achieve this purpose, a number of new fluorine-containing monomers were prepared and characterized.

This report was prepared by Eugene C. Stump and Calvin D. Padgett, both of Peninsular ChemResearch, Inc., under U. S. Army Contract DA19-129-AMC-152(N), with Mr. Charles B. Griffis and Mr. Frank H. Babers as project supervisors for the Army. E. C. Stump served as project director for Peninsular ChemResearch. Other workers at Peninsular ChemResearch who contributed to this research are Ward H. Oliver, Larry Sapp, Charles B. Wetzel, and Roy Higgenbotham.

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ABSTRACT

This report describes work carried out in the area of nitroso polymers. Two general classes were investigated. These were (1) sulfur-containing nitroso polymers and (2) nitroso polymers containing functional groups.

Synthesis of a wide variety of fluorine-containing nitroso compounds and olefins is described, as well as the synthesis of various fluorine-containing intermediates.

Nitroso copolymers and terpolymers were prepared containing functional groups such as halogen, ester, double bonds, and methoxy. Properties of selected systems are described.

A terpolymer which could be cross-linked by peroxide was prepared using methyl 4-nitrosoperfluorobutyrate as the termonomer.

Infrared spectra and NMR analysis of the new monomers and polymers are included.

I. INTRODUCTION

As part of its program on the development of materials for use in extreme environmental conditions, the U. S. Army Natick Laboratories (NLABS) has sponsored several research projects in the area of so-called nitroso rubber, a copolymer of trifluoronitrosomethane and tetrafluoroethylene.

This copolymer was first described by Barr and Haszeldine,[1] who reported that CF_3NO and $CF_2=CF_2$ reacted readily to give perfluoro-2-methyl-1,2-oxazetidine and a colorless, viscous oil which was identified as a 1-to-1 alternating copolymer.

$$CF_3NO + CF_2=CF_2 \longrightarrow CF_3N(-CF_2-CF_2-)O + \left(-NOCF_2CF_2-\right)_n \quad (CF_3)$$

Formation of the polymer was favored by a low temperature, liquid phase reaction. Russian workers[2] had earlier reported polymer formation in the reaction of nitrosyl chloride with 1,1-difluoro-2-chloroethylene. Although this polymer probably resulted from reaction of the olefin with the initial product, $CF_2ClCHClNO$, or its dehydrofluorinated derivative, $CFCl=CClNO$, its structure was not elucidated and was not shown to contain the $-N-O-(C)_x-$ repeating unit found in nitroso polymers.

$$ClNO + CF_2=CHCl \longrightarrow CF_2ClCHClNO$$

$$CF_2ClCHClNO \longrightarrow HF + CFCl=CClNO$$

$$CF_2ClCHClNO \text{ and/or } CFCl=CClNO + CF_2=CHCl \longrightarrow \text{polymer}$$

The copolymer reported by Haszeldine was found to be unaffected by hot concentrated sulfuric acid and potassium hydroxide.[1] In addition, the polymer chain contained heteroatoms which might confer good low temperature flexibility. On the basis of this information a research program was initiated in 1957 by the U. S. Army at Minnesota Mining and Manufacturing Company (3M) to study the preparation and properties of polymers derived from fluorine-containing nitroso compounds and fluoroölefins.[3,4] Although a wide variety of polymers was studied under this program, the $CF_3NO/CF_2=CF_2$ system was given the greatest amount of attention. It was shown that, when high purity monomers were used, elastomeric gums could be obtained with molecular weights in excess of 1,000,000. The solvent resistance and low temperature properties (Tg = -51°) of the copolymer were also demonstrated.

To evaluate the copolymer more extensively and investigate end-use applications, a program was initiated at Reaction Motors Division of Thiokol Chemical Corporation in 1963. Under this contract a method of producing high purity trifluoronitrosomethane at a rate of about 25 pounds per day was developed and 200 pounds of the copolymer were produced.[5]

The research program at Peninsular ChemResearch was also started in 1963. The initial objective of this work was the incorporation of compounds containing sulfur into the nitroso polymer system. This objective was later modified so that the major portion of this research was concerned with the synthesis of new nitroso copolymers and terpolymers. The only known cure for the copolymer, cross-linking by triethylenetetramine and hexamethylene diamine carbamate,[6] caused scorching and sponging with consequent low tensile strength of the vulcanizate. For this reason the majority of the termonomers used in this work contained labile groups which might be capable of providing a new cross-linking site without the use of the standard amine cure. The search for potential termonomers necessitated a major effort in the area of monomer synthesis. Both nitroso compounds and substituted fluoro-olefins were investigated as termonomers. Certain monomers were also supplied by the University of Florida and the University of Colorado under contracts directed by Professor Paul Tarrant and Professor J D Park, respectively.

A complete description of the work sponsored by the U. S. Army Natick Laboratories in this field has been presented by Henry and Griffis.

II. DISCUSSION

A. Monomer Synthesis

To prepare new nitroso polymers, it was frequently necessary to synthesize both new and previously reported fluorine-containing monomers and intermediates. Since these compounds varied greatly in structure and in functional groups, a discussion of their preparation will be divided into sections according to the characteristic feature of the individual compounds. For convenience, the following classifications have been selected:

1. sulfur-containing compounds
2. fluoroaromatic compounds
3. nitroso-esters and derivatives
4. trifluoronitrosomethane and other nitroso compounds
5. intermediates and miscellaneous compounds

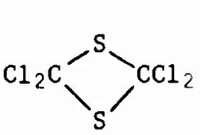
Physical properties and analyses of the new compounds prepared are listed in Table II. A reference to both the infrared and NMR spectra of these compounds is included in this table. These spectra are described in Appendix A and B, respectively. Parentheses, e.g. (A1), after a compound name or formula indicate that its infrared spectrum is shown in Appendix A.

1. Synthesis of Sulfur-Containing Compounds

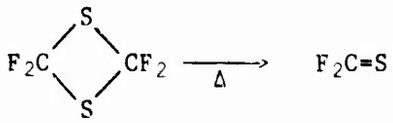
The initial research carried out under this program was directed toward the preparation of nitroso polymers containing sulfur. This objective, it was felt, might be accomplished by polymerization using either (a) a monomer which would incorporate sulfur in the backbone of the polymer or (b) a monomer which would result in a pendent group containing sulfur. In the latter case either a sulfur-containing olefin or nitroso compound might be used.

In order to investigate method (a), small quantities of thiocarbonyl fluoride and perfluorothioacetone were prepared. These compounds were synthesized using reported procedures, as shown. Due to the tendency

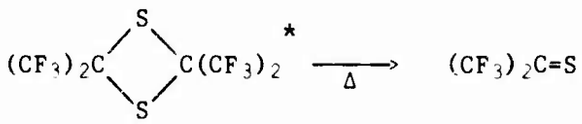
Thiocarbonyl Fluoride[8]

1. $Cl_2C{=}S \xrightarrow{u.v.}$ 

2.  (A1)

3.  (A2)

Perfluorothioacetone[9]

 (A3)

of these compounds to polymerize or cyclize, it was necessary to store them in acid-washed glass ampoules at -78°. Although the dithietane precursor to thiocarbonyl fluoride was washed until colorless with sodium hydroxide and hydrogen peroxide prior to distillation, this treatment is not strictly necessary and results in handling losses. It was later found that distillation of the crude dithietane results in samples of greater than 98% purity.

The investigation of polymerization using method (b) required the synthesis of both olefins and nitroso compounds. The previously unreported trifluoromethyl trifluorovinyl sulfide was prepared by the addition of trifluoromethanesulfenyl chloride to chlorotrifluoroethylene followed by dechlorination of the product mixture as shown. The addition

Trifluoromethyl Trifluorovinyl Sulfide[10] (A4)

1. $CCl_3SCl + NaF \xrightarrow{TMS} CF_3SCl + CF_3SSCF_3$ [11]

2. $CF_3SCl + CF_2{=}CFCl \xrightarrow{u.v.} CF_3SCFClCF_2Cl + CF_3SCF_2CFCl_2$ [12]

3. $CF_3SCFClCF_2Cl/CF_3SCF_2CFCl_2 \xrightarrow[\text{Dioxane}]{Zn} CF_3SCF{=}CF_2 + CF_3SCF_2CFCl_2$

of CF_3SCl to the olefin (step 2) was accomplished using a modification of the procedure described by Harris.[12] Whereas Harris carried out the addition by irradiation in the liquid phase, our reaction was run in the gas phase. This variation apparently results in a different product

---

* A sample of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane was provided by C. G. Krespan of DuPont, Wilmington, Delaware.

distribution. Harris reports a ratio of 78:22 (by GLC) while a ratio of 57:43 $CF_3SCFClCF_2Cl$:$CF_3SCF_2CFCl_2$ was determined by NMR for the mixture produced by gas-phase irradiation. Dechlorination using zinc in dioxane gave $CF_3SCF{=}CF_2$ conversions as high as 83%. The structure was verified by infrared, NMR analysis, and molecular weight determination. Pure (95%) $CF_3SCF_2CFCl_2$(A5) could also be distilled from the product mixture. Since separation of the isomers could not be achieved by distillation or GLC,[12] this method provides a relatively simple means of obtaining this compound.

Trifluorovinylsulfur pentafluoride, $CF_2{=}CFSF_5$, was prepared by a reported procedure[13] using the following sequence of reactions:

Trifluorovinylsulfur Pentafluoride (A6)

1. $SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl$ [14]

2. $SF_5Cl + CF_2{=}CFH \xrightarrow[CCl_4]{Bz_2O_2} CF_2ClCFHSF_5$

3. $CF_2ClCFHSF_5 \xrightarrow{KOH} CF_2{=}CFSF_5$

An attempt to add SF_5Cl to $CF_2{=}CFH$ (step 2) using ultraviolet irradiation in the gas phase produced no adduct. Reaction in an autoclave using benzoyl peroxide in carbon tetrachloride did, however, give reasonable conversions (58%). The dehydrochlorination reaction (step 3) was carried out using powdered potassium hydroxide in hexane solvent.

Several methods were investigated for the synthesis of highly fluorinated, sulfur-containing nitroso compounds, previous examples of which had not been found in the literature. The first compound in this class was prepared by the addition of nitrosyl chloride to trifluoromethyl trifluorovinyl sulfide as shown:

2-Chloro-1-nitroso-1,2,2-trifluoroethyl Trifluoromethyl Sulfide (A7)

$$CF_3SCF{=}CF_2 + ClNO \xrightarrow{u.v.} CF_3SCF(NO)CF_2Cl$$

A similar attempt to add nitrosyl chloride to $CF_2{=}CFSF_5$ by ultraviolet irradiation in the gas phase was not successful. When the reaction was carried out in dimethylformamide and $AlCl_3$, a nitroso compound, identified as $CF_2ClCFClNO$, was produced. Formation of this compound indicates a cleavage of the sulfur-carbon bond with intermediate formation of $CF_2{=}CFCl$, which then adds nitrosyl chloride to give the observed product.

A number of methods to synthesize nitrosylsulfur pentafluoride, SF_5NO, were examined without success. These methods included:

1. reaction of disulfur decafluoride with nitric oxide using both thermal activation and electric discharg

$$S_2F_{10} + NO \longrightarrow SF_5NO$$

2. reaction of disulfur decafluoride with nitrosyl chloride in solution

$$S_2F_{10} + ClNO \longrightarrow SF_5NO + SF_5Cl$$

3. reaction of sulfur tetrafluoride with nitrosyl fluoride

$$SF_4 + FNO \longrightarrow SF_5NO$$

4. reaction of cesiumsulfur pentafluoride with nitrosyl chloride

$$CsSF_5 + ClNO \longrightarrow SF_5NO + CsCl$$

5. reaction of sulfur chloride pentafluoride with nitric oxide using benzoyl peroxide

$$SF_5Cl + NO \longrightarrow SF_5NO$$

6. reaction of dinitrogen trioxide with sulfur tetrafluoride and cesium fluoride

$$SF_4 + CsF \longrightarrow [CsSF_5] + N_2O_3 \longrightarrow SF_5NO$$

Several previous attempts, all unsuccessful, to prepare SF_5NO have been reported. For example, a mixture of disulfur decafluoride[5] and nitric oxide was irradiated by ultraviolet light in the gas phase without formation of the desired product.[15,16] Since S_2F_{10} is known to cleave homolytically at 150° to give $\cdot SF_5$ radicals, the thermally activated reactions with S_2F_{10} were carried out at this temperature. The products of the reaction between S_2F_{10} and NO in glass were identified as NO_2, SOF_2, SO_2F_2, and SF_5OSF_5, while reaction in steel produced N_2O, SOF_2, SO_2F_2, and SF_4.

The reaction of SF_4 and nitrosyl fluoride at 300-400° in a nickel cylinder produced SOF_4, NO, SF_6, N_2O, SO_2F_2, SOF_2, NO_2, and SO_2.

The reaction of nitrosyl chloride with $CsSF_5$ at room temperature in glass gave, in addition to SF_5Cl, NO_2, SiF_4, SOF_2, SO_2F_2, and SF_4. A similar reaction, using dinitrogen trioxide rather than nitrosyl chloride, produced SOF_2 and SO_2F_2.

Since alkyl nitroso compounds may be prepared by pyrolysis or photolysis of the acyl nitrite,[23] as shown, it was proposed that

$$R_fCOONO \xrightarrow[\Delta]{u.v. \text{ or}} R_fNO + CO_2$$

SF_5NO might be synthesized by the series of reactions below. This method

1. $SF_5Cl + CH_2{=}CH_2 \longrightarrow SF_5CH_2CH_2Cl$ [24]

2. $SF_5CH_2CH_2Cl + KOH \longrightarrow SF_5CH{=}CH_2$ [24]

3. $SF_5CH{=}CH_2 \xrightarrow{ox.} SF_5COOH$

4. $SF_5COOH \xrightarrow{-H_2O} (SF_5CO)_2O$

5. $(SF_5CO)_2O + N_2O_3 \longrightarrow SF_5COONO$

6. $SF_5COONO \xrightarrow[or\ \Delta]{u.v.} SF_5NO + CO_2$

could not be evaluated, however, due to difficulties in preparing SF_5COOH (step 3). In addition to oxidation of $SF_5CH{=}CH_2$, other methods of preparing the acid were examined without success.

1. $SF_4 + COF_2 \xrightarrow{CsF} SF_5\overset{O}{\overset{\|}{C}}F \xrightarrow{H_2O} SF_5COOH$

2. $SF_5Cl + BuLi \xrightarrow[H^+]{CO_2} SF_5COOH$

Since the failure to detect SF_5NO as a product of these reactions may have been due to an inherent instability of the compound under the conditions employed, an attempt was made to produce "hot" SF_5 and NO radicals by passing a mixture of S_2F_{10} and nitric oxide through an electric discharge (Figure 1). The reaction was carried out both at ambient temperature and at -78°. At ambient temperature, identified

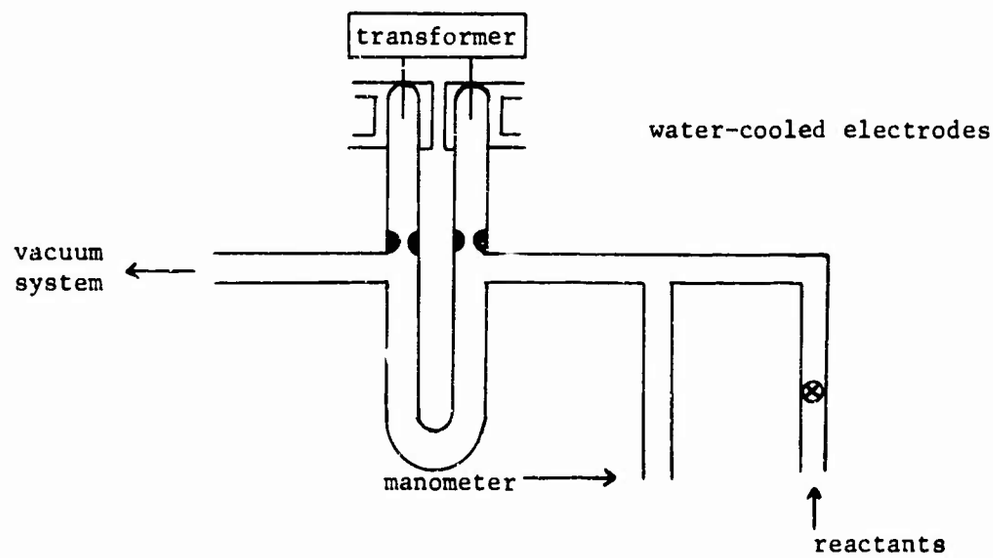


Figure 1. Electric Discharge Apparatus

products were SiF_4, N_2O, SO_2, SOF_2, SF_6, $SF(SO_3F)_2$, CF_4, CF_3Cl, and SF_5Cl. The last three compounds probably resulted by reaction with the Kel-F grease used on the joints in the discharge apparatus. At -78°, in addition to these same compounds, SO_2F_2 and SOF_4 were formed. In both cases an unidentified compound was isolated. From its infrared spectrum it appeared to contain an $-SO_2-$ group as well as SF bonds. No further efforts were made to identify this compound.

The various reactions used in the attempted synthesis of SF_5NO are described more fully in the experimental section.

The synthesis of SF_5CF_2COOH as a possible precursor to SF_5CF_2NO was also desired. Since the reaction of SF_5Cl with ketene has been reported to give SF_5CH_2COCl,[25] the reaction sequence below might give the the desired intermediate. Although difluoroketene has reportedly[26] been

1. $SF_5Cl + CF_2=C=O \longrightarrow SF_5CF_2COCl$

2. $SF_5CF_2COCl + H_2O \longrightarrow SF_5CF_2COOH$

prepared by reaction of $CF_2ClCOBr$ with zinc in ether, attempts to repeat this synthesis gave none of the desired ketene. Similar unsuccessful attempts by both English[27] and Russian[28] workers were subsequently reported.

In the initial phase of this contract, one of the classes of sulfur-containing monomers, which was desired for our polymerization studies, was thionitrites, R_fSNO, where R_f could be a perfluoroalkyl or perfluoroaryl group. Although the hydrocarbon analogues, RSNO, had been reported,[19] there was no mention in the literature of a successful synthesis of a perfluoroalkylthionitrite, R_fSNO. An unsuccessful attempt to prepare trifluoromethylthionitrite, CF_3SNO, had been described by Emeleus and Pugh,[20] who reacted bis(trifluoromethylthio)mercury with nitrosyl chloride. Instead of the thionitrite, the major product was the disulfide.

$$(CF_3S)_2Hg + 2ClNO \longrightarrow CF_3SSCF_3 + HgCl_2 + 2NO$$

In our laboratories a similar synthesis using trifluoromethylthiosilver and nitrosyl chloride gave similar results.

$$2CF_3SAg + 2ClNO \longrightarrow CF_3SSCF_3 + 2AgCl + 2NO$$

Since the disulfide seemed to be the favored product in reactions of this type, the reaction of CF_3SSCF_3 with nitric oxide was attempted. The disulfide can be cleaved homolytically by ultraviolet irradiation to give trifluoromethylthio radicals[21,22] so that a coupling reaction might give the desired product as shown.

$$CF_3SSCF_3 \xrightarrow[\text{r.t.}]{\text{u.v.}} CF_3S\cdot \xrightarrow{NO} CF_3SNO$$

Instead of the thionitrite, the major product of this reaction was found to be CF_3NO, formed in 38% conversion. Sulfur was also formed. Apparently, the trifluoromethylthio radicals decompose under these conditions to give trifluoromethyl radicals which then combine with nitric oxide.

$$CF_3SSCF_3 \xrightarrow{u.v.} CF_3S \qquad S + CF_3\cdot \xrightarrow{NO} CF_3NO$$

Some bis(trifluoromethyl)sulfide was also formed, indicating a combination of $CF_3S\cdot$ and $CF_3\cdot$ radicals. At lower temperatures (-78°), CF_3SCF_3 was the only product.

The reaction of CF_3SCl, which also cleaves homolytically to give a $CF_3S\cdot$ radical,[12] with excess nitric oxide produced a red solid when the reactants were condensed and frozen. This color existed only in the solid phase and could be regenerated by refreezing. The red color was probably not due to nitrosyl chloride since this compound was not detected in the reaction mixture on warming to room temperature, suggesting that CF_3SNO was formed in a solid matrix and is unstable under normal conditions. The few known thionitrites which have been reported[17-19] (RSNO, where R=CH_3, C_2H_5, C_6H_5) are described as red, relatively unstable liquids.

Reaction of both CF_3SCl and CF_3SSCF_3 with nitrosyl chloride resulted in products (CF_3Cl, CF_3NO_2) which showed that carbon-sulfur bond cleavage occurs rather easily in the $CF_3S\cdot$ radical to give sulfur and a $CF_3\cdot$ radical.

An attempt to react thiocarbonyl fluoride with nitrosyl fluoride, as shown, gave inconclusive results. An infrared spectrum

$$F_2C{=}S + FNO \longrightarrow CF_3SNO$$

of the volatile product mixture, which was found to contain SiF_4, COS and N_2O, exhibited absorption peaks between 8 and 9.2 microns and at 13.17 microns, indicating a CF_3S group. Other unassigned peaks occurred at 6.15, 6.25 and 6.52 microns. Although the peak at 6.52 can probably be attributed to carbon disulfide, the other two peaks are in the region in which typical highly fluorinated nitroso compounds absorb. This spectrum changed over a period of time, indicating decomposition of the sample at room temperature. Due to the difficulty in preparing thiocarbonyl fluorides, this method was not investigated further.

The synthesis of pentafluorophenyl thionitrite, C_6F_5SNO, was attempted using a procedure similar to that reported for the preparation of alkyl thionitrites, as shown.

$$C_6F_5SH + ClNO \not\longrightarrow C_6F_5SNO + HCl$$

At -40° a solid identified as bis(pentafluorophenyl)disulfide (A8) was formed in quantitative yield. Known thionitrites have been found to form the corresponding disulfides very readily at room temperature so that C_6F_5SNO, if formed, was converted under these conditions to the disulfide as shown.

$$2C_6F_5SNO \longrightarrow 2NO + C_6F_5SSC_6F_5$$

2. Synthesis of Fluoroaromatic Compounds

Fluorine atoms in pentafluorophenyl derivatives, C_6F_5R, may be displaced by nucleophilic reagents to give disubstituted products.[29,30] Substitution is generally directed to the position para to the R group.[31] Consequently, the incorporation of pentafluoroaromatic compounds into nitroso polymer would offer a potential cross-linking site. Functional groups capable of cross-linking would also be of interest as substituents on a perfluoroaromatic monomer.

The synthesis of pentafluoronitrosobenzene was carried out initially by a reported procedure,[32] as shown. Yields were generally around 40%.

Pentafluoronitrosobenzene (A9)

$$C_6F_5NH_2 + HCOOH/H_2O_2 \xrightarrow{CH_2Cl_2} C_6F_5NO$$

The product could be purified by distillation at reduced pressure and by sublimation to give blue crystals, m.p. 44-45°. The major by-product was found to be $C_6F_5NO_2$. The synthesis of C_6F_5NO by several other routes, shown below, was also examined, but without success. Only the third method gave any indication of the formation of the nitroso compound.

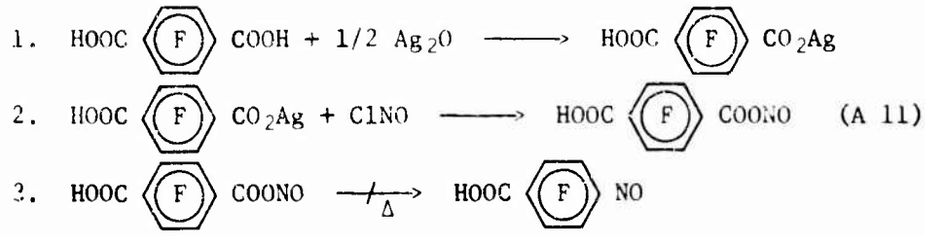
1. $C_6F_5NHN{=}C(CH_3)C_6H_5 + HCOOH/H_2O_2 \not\longrightarrow C_6F_5NO$

2. $C_6F_5H + BuLi \longrightarrow C_6F_5Li \xrightarrow{ClNO} \not\longrightarrow C_6F_5NO$

3. $C_6F_5COOAg + ClNO \longrightarrow C_6F_5COONO \xrightarrow[\Delta]{} C_6F_5N$

Pentafluorobenzoyl nitrite (A 10) was prepared and isolated as an amber liquid. Although pyrolysis of the nitrite gave inconclusive results, a sample sealed in an NMR tube at room temperature under partial vacuum formed a green solid believed to be C_6F_5NO.

Decomposition of the aryl nitrite was also used in attempts to prepare p-nitrosotetrafluorobenzoic acid. The monosilver salt of tetrafluoroterephthalic acid was prepared by reaction of the dicarboxylic acid with silver oxide. Reaction of the silver salt with nitrosyl chloride gave

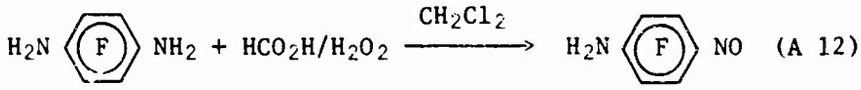


(A 11)

a product mixture from which a yellow, crystalline product, believed to be the mononitrite, was sublimed. Evidence for this structure was obtained by infrared analysis and by its hydrolysis with water to form nitric oxide and tetrafluoroterephthalic acid. Heating the nitrite at 200° under vacuum produced no noticeable color change. Subsequent to this work, the synthesis of p-nitrosotetrafluorobenzoic acid by another method was reported.[33]

The synthesis of p-aminotetrafluoronitrosobenzene was accomplished, as shown, by the performic acid oxidation of 1,4-diaminotetra-

p-Aminotetrafluoronitrosobenzene



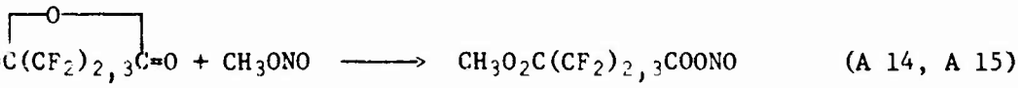
(A 12)

fluorobenzene. The product, after separation from the reaction mixture by sublimation, was a green solid which gave a green solution with methylene chloride. Further evidence for its structure was obtained by infrared analysis, which shows a peak near 1555 cm^{-1} attributed to N-O absorption,[33] as well as N-H peaks below 3 microns. In addition, the compound reacted with tetrafluoroethylene to give a solid polymer whose infrared spectrum showed peaks attributable to N-H, C-F, and fluoro-aromatic absorption.

The oxidation of 4,4'-diaminooctafluorobiphenyl was also attempted using performic acid. Although a yellow solid was obtained in good yield, it was not identified. Its infrared spectrum (A 13) indicates that it still contains N-H bonds.

3. Synthesis of Nitroso-Esters and Derivatives

The previously unreported reaction of both perfluorosuccinic and perfluoroglutaric anhydrides with methyl nitrite was found to produce a nitrite-ester, as shown. The reaction occurs easily and exothermically



(A 14, A 15)

to give near-quantitative yields. Structure of the two nitrite-esters was established by NMR, elemental and infrared analysis. The infrared spectra show typical methyl, nitrite, and ester absorption, as well as strong C-F absorption.

The nitrite-esters were decarboxylated by both pyrolysis and ultraviolet irradiation, as shown, to give the corresponding nitroso-

$$CH_3O_2C(CF_2)_{2,3}COONO \xrightarrow[\Delta]{U.V. or} CO_2 + CH_3O_2C(CF_2)_{2,3}NO \quad \text{(A 16, A 17)}$$

esters. Conversions ranged from about 20% to 47% with the average conversion from over ten reactions close to 21%. The compounds were identified by NMR, elemental, and infrared analysis. The blue liquid nitroso-esters were purified by distillation at low pressures to give high-purity (>99%) monomers. Due to the high cost of perfluorosuccinic anhydride, most of the reactions were carried out with the perfluoroglutaric anhydride derivatives.

Decarboxylation by pyrolysis was generally carried out at about 250°* by either dropping the nitrite-ester into a packed, heated column under vacuum or by dropping the nitrite-ester into a heated pot at the bottom of a heated column under vacuum and removing the product from the top. In the latter procedure a distillation head was placed on the column to withdraw non-volatile products. In the pyrolysis of both nitrite-esters appreciable amounts of colorless, high-boiling liquid were obtained. The high boiling liquid produced in the pyrolysis of $CH_3O_2C(CF_2)_3COONO$ was identified by NMR, elemental, and infrared analysis as the triester, $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$ (A 18). This compound could be formed by the following reactions:

$$CH_3O_2C(CF_2)_3NO \xrightarrow[\Delta]{U.V. or} NO + CH_3O_2C(CF_2)_3\cdot$$

$$CH_3O_2C(CF_2)_3\cdot + CH_3O_2C(CF_2)_3NO \longrightarrow [CH_3O_2C(CF_2)_3]_2NO\cdot$$

$$[CH_3O_2C(CF_2)_3]_2NO\cdot + CH_3O_2C(CF_2)_3\cdot \longrightarrow [CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$$

A similar compound, $(C_3F_7)_2NOC_3F_7$, has been obtained by the pyrolysis or photolysis of C_3F_7NO [22]. High-boiling liquid formed in the pyrolysis of $CH_3O_2C(CF_2)_3COONO$ was subsequently identified by NMR and infrared analysis as $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_2CO_2CH_3$ (A 19).

Decarboxylation of the nitrite-esters to nitroso-esters could also be accomplished by ultraviolet irradiation. Photolysis also produced the high-boiling liquids mentioned above. Both methods give approximately the same conversions, but the photolytic decomposition is preferred since it requires less attention and regulation.

Attempts to increase the conversion to nitroso-ester by passage of pure nitric oxide through the pyrolysis tube at 5 mm. pressure were not successful.

---

*Pyrolysis at higher temperatures (350°-400°) results in the formation of a high-boiling purple liquid, possibly a nitroxide.

The triester by-product was converted to the triamide and trinitrile, as shown,

$$[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3 \xrightarrow{NH_3} [H_2NC(CF_2)_3]_2NO(CF_2)_3CNH_2 \quad (A20)$$

$$[H_2NC(CF_2)_3]_2NO(CF_2)_3CNH_2 \xrightarrow{P_2O_5} [NC(CF_2)_3]_2NO(CF_2)_3CN \quad (A21)$$

which were identified by NMR, elemental and infrared analysis.

An initial attempt to synthesize a nitroso-ester by pyrolysis of a nitrite-ester, prepared by the reaction of a monosilver salt with

$$O{=}C\overset{\overset{O}{\frown}}{CF_2CF_2}C{=}O + CH_3OH \longrightarrow CH_3O_2CCF_2CF_2COOH$$

$$CH_3O_2CCF_2CF_2COOH + Ag_2O \longrightarrow CH_3O_2CCF_2CF_2CO_2Ag$$

$$CH_3O_2CCF_2CF_2CO_2Ag + ClNO \longrightarrow AgCl + CH_3O_2CCF_2CF_2COONO$$

$$CH_3O_2CCF_2CF_2COONO \xrightarrow[\Delta]{} CH_3O_2CCF_2CF_2NO$$

nitrosyl chloride, produced a volatile blue liquid. This approach was not pursued, however, due to the concurrent discovery of the more facile method previously discussed.

The attempted synthesis of $CH_2{=}CHCH_2O_2C(CF_2)_3COONO$ by reaction of allyl nitrite with perfluoroglutaric anhydride resulted in a vigorous, exothermic reaction and, in one case, a detonation. When the reaction was carried out at 0° in an open system, a viscous, dark brown material was obtained. Infrared analysis showed that this material was not the desired nitrite-ester.

The synthesis of $ClOC(CF_2)_{2,3}COONO$ was attempted to provide a precursor to nitroso acids. No evidence of reaction was obtained,

$$O{=}C\overset{\overset{O}{\frown}}{(CF_2)_{2,3}}C{=}O + ClNO \not\longrightarrow ClOC(CF_2)_{2,3}COONO$$

$$ClOC(CF_2)_{2,3}COONO \xrightarrow[\Delta]{U.V.\text{ or}} \xrightarrow{H_2O} HOOC(CF_2)_{2,3}NO$$

however, when the reactants were mixed at room temperature or irradiated by ultraviolet light. Samples of 4-nitrosoperfluorobutyric acid (A22) were subsequently prepared both by a reported procedure[4] and by the hydrolysis of methyl 4-nitrosoperfluorobutyrate.

$$CH_3O_2C(CF_2)_3NO \xrightarrow{H_2O} HOOC(CF_2)_3NO$$

Hydrolysis can be accomplished using water, acid, or dilute (0.1 N) base. When a stronger (5% NaOH) base was used, the blue color of the nitroso compound faded after 10 minutes at room temperature. Consequently, neutral or acidic hydrolysis is preferred. The blue product was then isolated

either by extraction or by salting out with sodium chloride and then dried. Although hydrolysis occurs more rapidly in acidic media (1 day) than in neutral media (4-5 days), conversions as high as 75% were obtained with the latter method.

4. Synthesis of Trifluoronitrosomethane and Other Nitrosoalkanes

In the initial stage of this contract it was necessary to prepare working quantities of trifluoronitrosomethane in the laboratory. Subsequently, this compound was made available from stock. The procedure used for this synthesis was as follows:

$$(CF_3CO)_2O + N_2O_3 \longrightarrow 2CF_3COONO \quad ^{37}$$

$$CF_3COONO \xrightarrow{\Delta} CF_3NO + CO_2 \quad ^{38}$$

Pyrolysis of trifluoroacetyl nitrite, which was obtained in nearly quantitative yield as reported, was accomplished by dropping into refluxing FC-43 (3M Co.).[5] The volatile products were purified by scrubbing with 5-7% KOH and passage through a column packed with Linde 4A Molecular Sieve at -78° The major impurities - CO_2, $(CF_3)_2NOCF_3$, CF_3NO_2, and nitrogen oxides - are removed by this procedure to give CF_3NO of purity in excess of 99%. Conversions after purification averaged about 50%. The results of nine small scale experiments are summarized in Table I. Using the apparatus described in the Experimental section, about 120 g. of CF_3NO could be prepared in one day. About 1 Kg. of pure CF_3NO was prepared before it became available from stock.

TABLE I

SYNTHESIS OF CF_3NO

Run No.	CF_3COONO (grams)	Addition Time (Hrs.)	Yield of CF_3NO (grams)	(%)	Remarks
1	125	6	48	55	
2	80	3	29	53	
3	172	7.5	51	45	Nitrite not of sufficient purity, contained NO_2
4	140	6	48	49	
5	80	3	35	63	
6	65	3	22	49	
7	230	9	74	45	
8	200	6	43	31	Equipment failed, lost some nitrite.
9	143	6	43	43	Equipment failed, leak in purifying train, lost CF_3NO before discovering leak.

A detailed description of the synthesis of CF_3NO on a larger scale (~1 lb./hr.) may be found elsewhere.[5,7]

1-Bromo-1,1,2,2-tetrafluoro-2-nitrosoethane was prepared by the ultraviolet-catalyzed, vapor phase addition of nitrosyl bromide to tetrafluoroethylene. In addition to the desired product, a small amount

$$BrNO + CF_2{=}CF_2 \xrightarrow{U.V.} CF_2BrCF_2NO \qquad (A23)$$

of CF_2BrNO was also formed. This compound could result from addition of nitrosyl bromide to difluoromethylene or by carbon-carbon bond cleavage followed by combination with NO or Br. NMR analysis of CF_2BrCF_2NO is given in Appendix B.

Methyl 1-chloro-1,2,2-trifluoro-2-nitrosoethyl ether, $CH_3OCFClCF_2NO$, was prepared by the addition of nitrosyl chloride to methyl trifluorovinyl ether.[39] The addition is carried out in CF_2Cl_2 at -78° and

$$ClNO + CH_3OCF{=}CF_2 \longrightarrow CH_3OCFClCF_2NO \qquad (A24)$$

is unusually rapid. Another noteworthy aspect of this reaction is that the nitrosonium ion adds to the terminal difluoromethylene group to give a primary nitroso group. In most cases of addition of nitrosyl chloride to a fluoroölefin containing one group or atom other than fluorine attached to the olefinic carbon atoms, the nitroso group will attack the carbon atom with fewer fluorine atoms. For example, nitrosyl chloride adds to chlorotrifluoroethylene and perfluoropropylene, as shown. Assuming the

$$ClNO + CF_2{=}CFCl \longrightarrow CF_2ClCFClNO \quad [40]$$

$$ClNO + CF_3CF{=}CF_2 \longrightarrow CF_3CF(NO)CF_2Cl \quad [41]$$

addition of nitrosyl chloride to alkyl trifluorovinyl ethers to be ionic, the reversed nature of the addition might be explained by contribution of the structure resulting from donation of electrons to the system through the oxygen atom:

$$CH_3\ddot{O}CF{=}CF_2 \rightleftharpoons CH_3\overset{+}{O}{=}CFCF_2^{-}$$

An attempt has been made to prepare a functional nitroso compound by the reaction of 1,3-diiodohexafluoropropane with nitric oxide.

$$ICF_2CF_2CF_2I + NO \longrightarrow ICF_2CF_2CF_2NO$$

and/or $ONCF_2CF_2CF_2NO$

This reaction could give either an iodonitroso propane, which could be used as a reactive termonomer, or a dinitroso propane, which might be valuable as a cross-linking agent. This reaction was attempted both with and without mercury in the presence of sunlight, but no evidence for the formation of a nitroso compound was obtained in either case.

An attempt was made to prepare an unsaturated nitroso compound by reaction of methyl nitrite with perfluorobutadiene. Although no reaction was apparent in the absence of light, exposure to sunlight produced a light blue-green liquid, which rapidly lost its color during attempted purification. An infrared spectrum of this material showed C-H absorption as well as peaks which might be attributed to C=C, $-NO_2$, and -ONO groups. The desired reaction is shown below.

$$CH_3ONO + CF_2=CFCF=CF_2 \longrightarrow CH_3OCF_2CF=CFCF_2NO$$

$$\text{and/or } CH_3OCF_2\underset{\displaystyle NO}{\underset{|}{C}}FCF=CF_2$$

A similar reaction was also attempted using methyl nitrite and tetrafluoroethylene. The only nitroso compound isolated from the product mixture was identified as $ONCF_2CF_2NO_2$.

5. Synthesis of Intermediates and Miscellaneous Compounds

During the course of this contract it was necessary to prepare a wide variety of intermediates which were not commercially available. These compounds, for convenience, have been classified as sulfur-containing compounds, fluoroaromatic compounds, nitroso compound precursors, fluoroolefins, and miscellaneous. In some cases a particular synthesis was carried out several times and, in describing these in the Experimental section, a typical reaction or the reaction providing the best yield is given. References for each synthesis, when available, are also given.

B. Polymer Synthesis

Initial efforts under this contract were directed toward the incorporation of sulfur atoms into the nitroso system. This might be accomplished in either of two ways. First, by polymerization with a sulfur-containing nitroso compound or fluoroolefin as exemplified by Eq. 1 and 2, and second, by polymerization with a compound such as thiocarbonyl fluoride or hexafluoroethioacetone, as exemplified by Eq. 3. The latter method would give a polymer containing sulfur in the backbone.

1. $CF_2=CF_2 + R_{sf}NO \longrightarrow \left\{NOCF_2CF_2\right\}_n$ with R_{sf} on the CF group

2. $CF_3NO + CF_2=CFR_{sf} \longrightarrow \left\{NOCF_2CF\right\}_n$ (with CF_3 and R_{sf}) and/or

$\left\{NO-CFCF_2\right\}_n$ (CF_3, R_{sf})

3. $CF_3NO + (R_f)_2C=S \longrightarrow \left\{NO-CS\right\}_n$ (CF_3, R_f, R_f)

where R_{sf} = a sulfur-containing perfluoroalkyl group

R_f = fluorine and/or a perfluoroalkyl group

Although it was found that copolymers of thiocarbonyl fluoride and hexafluorothioacetone could not be prepared under normal conditions (only the homopolymer of the sulfur compound was formed), a copolymer of trifluoronitrosomethane and trifluoromethyl trifluorovinyl sulfide was prepared (Table IV, No. 15). The olefin appeared to be much less reactive than tetrafluoroethylene and a relatively low conversion and molecular weight were obtained. The glass transition temperature of the copolymer was found to be -48°, about that of the copolymer of CF_3NO and $CF_2=CF_2$. An infrared spectrum of this copolymer is shown in Appendix A (A26).

Small amounts of another sulfur-containing monomer, $CF_3SCF(NO)CF_2Cl$, were also incorporated as a termonomer but, due to the difficulty in obtaining adequate quantities of the monomer, this system was not examined further.

The second and major area of our polymerization work was concerned with the incorporation of monomers containing functional groups into the nitroso system. One of the major problems in the development of nitroso rubber was in finding an adequate means of curing it. Although a cure may be obtained using triethylenetetramine and hexamethylenediamine dicarbamate, the vulcanizates are generally weak and inconsistent in properties[5]

At the time this research was undertaken, very few nitroso terpolymers containing functional groups had been reported. Under an early NLABS-sponsored nitroso program at 3M, a terpolymer containing p-trifluorovinyl benzoic acid was prepared and cross-linked with barium hydroxide. Of more significance, however, was the preparation of a terpolymer containing either 3-nitrosoperfluoropropionic acid or 4-nitrosoperfluorobutyric acid.[illegible,58] The 3M researchers found that these terpolymers could be cured by metal salts such as chromium trifluoroacetate, diols, and diepoxides The chromium trifluoroacetate cured material was found to exhibit good tensile strength and elongation and had excellent resistance to N_2O , nitric acid, sulfuric acid, and sodium hydroxide.

As part of the work at PCR, we investigated the incorporation of both olefinic and nitroso monomers.

It was found that bromotrifluoroethylene would copolymerize readily with trifluoronitrosomethane to give a tough, almost insoluble gum in conversions in the order of 90% NMR and elemental analysis

$$CF_3NO + CF_2{=}CFBr \longrightarrow \left(\underset{\displaystyle CF_3}{N}OCF_2CFBr \right)_n \quad (A27) \qquad \text{90\% conversion, Tg } 3°$$

$$CF_3NO + CF_2{=}CF_2 + CF_2{=}CFBr \longrightarrow \left(\underset{\displaystyle CF_3}{N}OCF_2CF_2\underset{\displaystyle CF_3}{N}OCF_2CFBr \right)_n$$

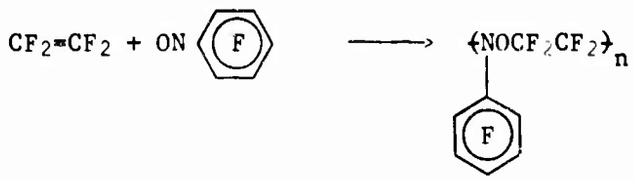
Charge (mmoles)			$CF_2{=}CFBr$ in polymer (mole %)	Tg	[η]*
35	29	6	9.4	-45	0.15
35	23	12	21.7	-35	0.13
35	17.5	17.5	31.0	-21	-

*In FC-43

indicated a 1-to-1 copolymer with the alternating structure shown in the first equation predominating. As in the case of the copolymer of CF_3NO with tetrafluoroethylene, about 15% "abnormal" addition was observed.

Intrinsic viscosities of the terpolymers were relatively low, possibly due to chain transfer process involving abstraction of a bromine atom from the olefin. As expected, the glass temperature rises with increasing amounts of BTFE, as shown. At 9 mole % the Tg is practically unchanged, but rises to 3° in the copolymer. These samples were found to decompose around 200°. By way of comparison, the decomposition temperature of $CF_3NO/CF_2=CF_2$ copolymer is about 270°. It was felt that this system might be cured by abstraction of bromine using a peroxide, but no cross-linking was observed using DiCup 40.[57]

A series of polymers containing pentafluoronitrosobenzene was also prepared as shown below. Incorporation of this compound drastically



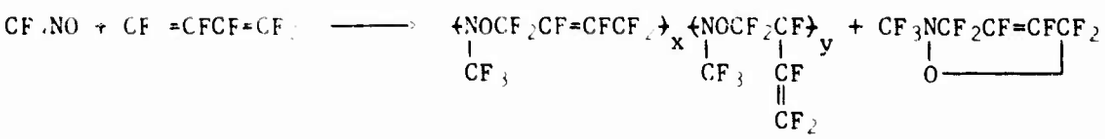
$$CF_3NO + CF_2=CF_2 + C_6F_5NO \longrightarrow \sim\sim NOCF_2CF_2NO\sim\sim \quad (A28)$$

(CF_3 and C_6F_5 substituents)

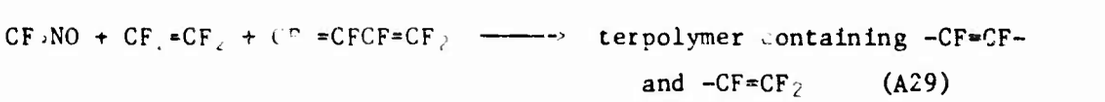
Charge (mole %)			T_g	T_d
47.5	50	2.5	-43	166
45.0	50	5.0	-39	158
40.0	50	10.0	-35	152

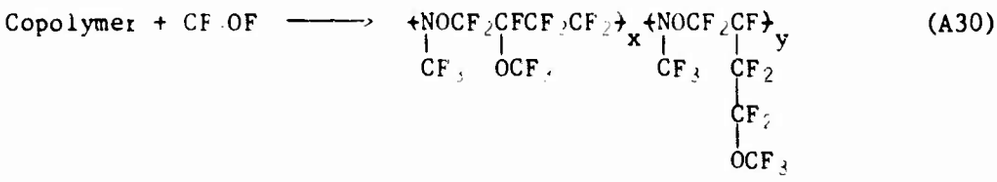
reduced the thermal stability of the system and raised the glass temperature. The terpolymer containing about 2.5 mole % pentafluoronitrosobenzene decomposed about 100° lower than the copolymer. Attempts to cross-link the terpolymer through the normally labile para fluorine atom were unsuccessful.[57]

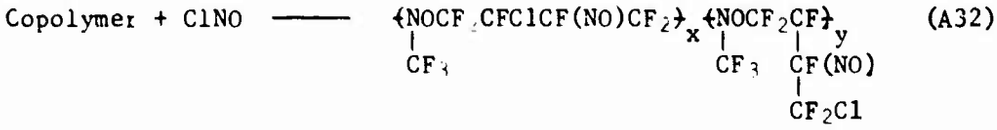
As shown below, a copolymer and terpolymers containing perfluorobutadiene were prepared. In all these polymerizations, appreciable quantities of the Diels-Alder adduct (A31) were formed. NMR and infrared analysis indicates that polymerization occurs by a 1,2 and 1,4 mechanism with the 1,4 predominating. An infrared spectrum of the terpolymer shows the trifluorovinyl group at 5.61 microns and the CF=CF group at 5.80 microns. About 5-10% of the diene undergoes 1,2 polymerization to give polymers containing a pendent trifluorovinyl group.



Tg = -43°





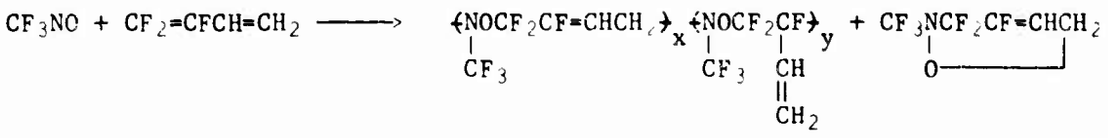


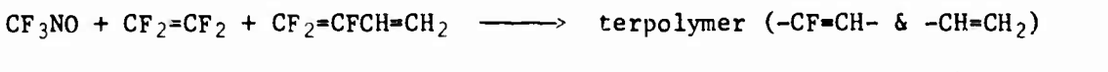
Blue polymer

Tg = -85°

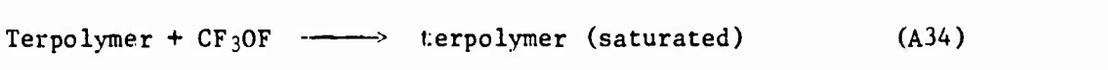
In order to determine the reactivity of the double bonds, both trifluoromethyl hypofluorite and nitrosyl chloride were added to the dissolved copolymer. NMR analysis of the CF_3OF adduct shown in the third equation again confirmed that the predominant structure was formed by 1,4 polymerization. The addition of nitrosyl chloride produced a light blue polymer whose infrared spectrum showed a peak at 6.2 microns. This may be attributed to the formation of nitroso groups as shown in the fourth equation. The glass temperature of this polymer was found to be -85°. Since the glass temperature of the copolymer is -43°, this unexpected value is difficult to explain. The addition of bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, to the terpolymer was also examined in an attempt to cross-link the polymer, but the results were inconclusive.

As shown below, polymers containing trifluorobutadiene were also prepared. As in the previous case, the 1,4 mechanism predominates and part of the monomer charge is consumed to give the Diels-Alder adduct. As before, the reactivity of the double bonds was demonstrated by the addition of CF_3OF to give a saturated terpolymer.





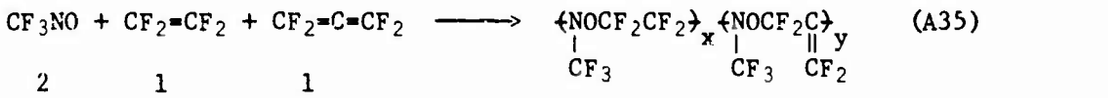
(A33)



(A34)

Attempts to cure the unsaturated terpolymers prepared from perfluorobutadiene and 1,1,2-trifluorobutadiene were unsuccessful.[57]

In addition to the polymers prepared from perfluorobutadiene and trifluorobutadiene mentioned previously, unsaturated nitroso polymers have been prepared, as shown below, by terpolymerization of CF_3NO and tetrafluoroethylene with tetrafluoroallene, difluoroallene, and 3-nitroso-perfluoropropene.

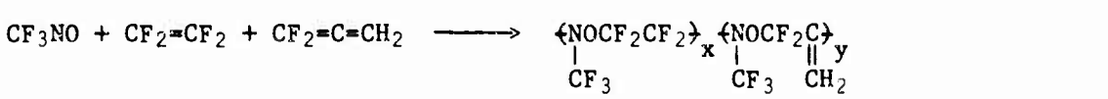


(A35)

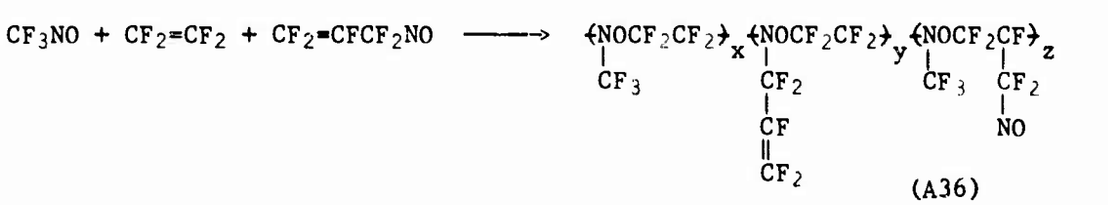
2 1 1

[η] = 0.13

Tg = -35°



dec. 70°



(A36)

A low molecular weight gum with an intrinsic viscosity of 0.13 was obtained using tetrafluoroallene. An infrared spectrum of the polymer showed a strong peak at 5.68 microns probably due to $C{=}CF_2$ absorption.

The terpolymer obtained from difluoroallene was found to decompose at 70 . A copolymer of difluoroallene with trifluoronitrosomethane decomposed rapidly at room temperature. The terpolymer with 3-nitroso-perfluoropropene gave, in addition to material soluble in Freon 113, a small amount of insoluble gel, indicating that some cross-linking had occurred. The infrared spectrum of the reprecipitated polymer exhibited strong absorption at 5.58 microns due to the double bond in the pendent perfluoroallyl group In addition, a peak at 6.2 microns indicates that some polymerization occurred through the trifluorovinyl group, giving pendent -CF NO groups.

Probably the most significant development during this work was the synthesis and polymerization of the nitroso esters, $CH_3O_2C(CF_2)_2NO$ and $CH_3O_2C(CF_2)NO$. Since the latter compound was more easily prepared and the starting anhydride less expensive, the majority of the polymerizations were carried out with this compound

As shown below, terpolymers containing the nitroso ester were

$$CF_3NO + CF_2{=}CF_2 + CH_3O_2C(CF_2)_2NO \longrightarrow$$

$$\left(\begin{array}{l} NOCF_2CF_2 \\ \quad | \\ \quad CF_3 \end{array}\right)_x \left(\begin{array}{l} NOCF\text{-}CF_2NO \\ \quad | \quad\quad | \\ \quad CF_3 \quad (CF_2)_2 \\ \quad\quad\quad\quad | \\ \quad\quad\quad CO_2CH_3 \end{array}\right)_y \qquad \text{(A37)}$$

Conditions: bulk, -30°, 24 hrs
Conversions: 70-80%
$[\eta]$ = 0.25 to 0.50

prepared containing from 2.5 to 10 mole % ester. Incorporation of the nitroso ester was established by infrared and NMR analysis. The polymers were elastomeric gums with the same appearance as the copolymer of $CF_3NO/CF_2{=}CF_2$ and could be cured using a standard peroxide cure developed at the Natick Laboratories The gum handles easily on the mill and shows no signs of scorching.

Finally, as shown below, a polymer of potential utility was prepared using trifluorovinyl methyl ether as a comonomer or termonomer.

$$CF_3NO + CH_3OCF{=}CF_2 \longrightarrow \left(\begin{array}{l} NOCF_2CF \\ \quad | \quad\quad | \\ \quad CF_3 \quad OCH_3 \end{array}\right)_n \text{ and/or } \left(\begin{array}{l} NO\text{-}CFCF_2 \\ \quad | \quad\quad | \\ \quad CF_3 \quad OCH_3 \end{array}\right)_n$$

67 mole % ether

insoluble in Freon 113 and FC-43

$$CF_3NO + CF_2{=}CF_2 + CH_3OCF{=}CF_2 \longrightarrow \text{Terpolymer} \qquad \text{(A38)}$$

5 4 1 $[\eta]$ = 0.64 (in FC-43)

The trifluorovinyl ether is extremely reactive with trifluoronitrosomethane, copolymerizing at -78° in a few hours. By comparison, tetrafluoroethylene and CF_3NO require periods of about one month at this temperature. In addition, elemental analysis indicates that the copolymer contains greater than 67 mole % ether. As far as can be determined, this is the first time a nitroso copolymer containing more or less than the equivalent amount of one of the monomers has been prepared.

The copolymer is a tough, colorless gum which is insoluble in Freon 113 and FC-43. A terpolymer containing about 10 mole % ether was soluble in FC-43 and had an intrinsic viscosity of 0.64. Attempts to cure the terpolymers using peroxide have to date been unsuccessful.[57]

Other copolymerizations and terpolymerizations, including unsuccessful attempts, are described in Tables III to VIII.

C NMR Analysis of $CF_2NO/CF_2=CF_2$ Copolymers

On the basis of NMR data, researchers at 3M[7] reported that a small percentage of "abnormal" linkages appear to be present in the nitroso polymer backbone. These abnormalities could result from a deviation in the normal head-to-tail structure to give linkages such as:

$$\text{-}(NOCF_2CF_2ON)\text{-} \quad \text{and} \quad \text{-}(ONCF\,CF_2NO)\text{-}$$
$$\quad\;\; | \qquad\quad | \qquad\qquad\;\; | \qquad\quad |$$
$$\quad CF_2 \qquad CF_2 \qquad\qquad CF_2 \qquad CF_2$$

NMR spectra of nitroso polymers prepared in our laboratories have consistently shown additional fluorine NMR peaks, occasionally in appreciable amounts. In addition to the normal peaks found at -12.0 (CF_3), +11.4 (CF_2) and +23.7 (CF_2) ppm with reference to trifluoroacetic acid, peaks are almost invariably found at +14.0 and +21.5 ppm. These peaks amount to anywhere from 14 to 16% of the area attributed to CF_2. Also, several polymers have shown additional CF_2 and CF_3 peaks suggesting not only abnormal linkages, but also the possibility that a certain amount of non-alternating polymerization may occur to give units such as:

$$\text{-}(NOCF_2CF_2CF\,CF_2)\text{-} \quad \text{and} \quad \text{-}(CF_2CF_2N\,O\,N\,O)\text{-}$$
$$\quad\;\; | \qquad\qquad\qquad\qquad\qquad\qquad\;\; | \qquad |$$
$$\quad CF_3 \qquad\qquad\qquad\qquad\qquad\qquad CF_2 \quad CF_3$$

Although these additional peaks may be due to higher molecular weight cyclic compounds, it has been definitely established that they are not due to dissolved oxazetidine, $CF_2\underline{NOCF_2CF_2}$. NMR results are summarized in Table IX. Another unusual observation can be made in that the total CF_3 content ranges from 41.7 to 58.0%. The peak area for CF_3 in an alternating 1-to-1 copolymer should be about 43%. Also, polymers prepared under practically identical conditions sometimes exhibited gross differences in spectra as exemplified by samples 78.4.2 and 78.5.2. It should be noted that the polymers listed in the table are all intentionally of relatively low molecular weight to allow the possible detection of end groups by NMR.

Due to the complexity of the problem of analyzing these polymers by NMR, and because of the increased interest in the functional terpolymer systems, this study was not pursued.

III. EXPERIMENTAL

A. Monomer Synthesis

1. Synthesis of Sulfur-Containing Compounds

a. Thiocarbonyl Fluoride[8]

2,2,4,4-Tetrafluorodithietane (4.0 g.) was added dropwise over a period of 15 minutes through a Pyrex pyrolysis tube consisting of a 12-inch Vigreaux column with a 6-inch heated zone. The tube was maintained at 520°-540° and a slow stream of nitrogen (25-30cc/min) was passed through the system during pyrolysis. Products were caught in traps at -183°. Trap to trap distillation indicated that an appreciable amount of material had passed through unreacted. The more volatile portion was primarily $F_2C{=}S$. An early attempt to store this material in stainless steel at room temperature resulted in decomposition. No difficulty was encountered, however, when the material was stored at -78° in a glass Fischer-Porter tube. The infrared spectrum of this compound is shown in Figure A2.

b. Perfluorothioacetone

Reaction of bis(perfluoroisopropyl) mercury with sulfur [9b]

Two attempts were made to prepare $(CF_3)_2CS$ from $[(CF_3)_2CF]_2Hg$ and sulfur. The first time a water-cooled condenser was used, and it soon plugged. In the second attempt, described below, an air-cooled tube one inch in diameter was used as a condenser.

A 1-liter, 4-neck flask was half filled with melted sulfur and fitted with a condenser, thermometer, stirrer, and addition funnel containing $[(CF_3)_2CF]_2Hg$. The sulfur was heated to its boiling point and the mercury compound slowly added. The condenser was vented through a trap cooled to -78°. Some blue material was caught, but after standing for several days it turned to a white solid and, on warming to room temperature, to a colorless liquid. Perfluorothioacetone is reported to be a blue liquid which easily dimerizes, and it appears that $(CF_3)_2CS$ was made in this reaction but dimerized during storage.

Pyrolysis of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane [9a]

Perfluorothioacetone was prepared by the pyrolysis of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane. An addition funnel containing $(CF_3)_2CSC(CF_3)_2S$ was connected to a 12-inch Vigreaux column heated to 600°C. The column was vented to a trap cooled to -78°. The dithietane was slowly dropped into the heated column as it was being swept with a stream of N_2. The product was trapped as a blue liquid. An infrared spectrum of the compound is shown in Figure A3.

c. Trifluoromethyl trifluorovinyl Sulfide

CF_3SCl

Sodium fluoride (400 g., 9.52 moles) and tetramethylenesulfone (1000 ml.) were placed in a 2-liter, 4-neck flask fitted with a thermometer, stirrer, spiral condenser, and addition funnel. The funnel contained CCl_3SCl (404 g., 2.19 moles) which was added to the reaction flask over a ten minute period. The contents of the flask were stirred and heated at 160-170°, and the volatile products were trapped at -78°. These products were distilled, and CF_3SCl* (89 g., b.p. 0°-9°) and CF_3SSCF_3* (69 g., b.p. 27°-34°) were obtained.

Trifluoromethanesulfenyl chloride was also prepared by the gas phase reaction of bis(trifluoromethyl) disulfide and chlorine. The disulfide (180 g., 0.891 mole) was bled into a 72-liter evacuated flask. Chlorine (68.06 g., 0.891 mole) was added and the mixture irradiated two hours by ultraviolet light using a Vycor immersion well. The product was removed and distilled to give CF_3SCl (204 g., 84% conversion).

$CF_3SCFClCF_2Cl$

A 72-liter flask was evacuated and charged with CF_3SCl (243 g., 1.78 moles) and $CF_2=CFCl$ (86 g., 0.74 mole) and irradiated for three hours by a Hanovia model 8A36 high-pressure mercury vapor lamp suspended in a Vycor immersion well extending into the flask. The products from two experiments were combined and distilled to give recovered CF_3SCl (220 g., 1.62 moles), material boiling near 44° (100 ml.) and assumed to be a mixture of CF_3SSCF_3 and $CF_2ClCFCl_2$, product (95.3 g.) boiling at 78°-83°, and pot residue (80 g.) assumed to be telomers with the composition $CF_3S(C_2F_3Cl)_nCl$. NMR analysis of the fraction boiling at 78°-83° showed it to be 57%* $CF_3SCFClCF_2Cl$ and 43% $CF_3SCF_2CFCl_2$.

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*These compounds have been reported to be highly toxic.

$CF_3SCF=CF_2$

1 l-liter, 3-neck flask was fitted with a stirrer, addition funnel and reflux condenser leading to a cold trap. The flask was charged with dioxane (500 ml.), powdered zinc (75 g.), and a trace of zinc chloride. The mixture was heated to reflux and a mixture of 57% $CF_3SCFClCF_2Cl$ - 43% $CF_3SCF_2CFCl_2$ (95.3 g. containing 0.215 mole $CF_3SCFClCF_2Cl$) was added over 90 minutes. Volatile material was caught in the cold trap and distilled using an 18-inch spinning band column. Material boiling from 13°-20° was collected with the major fraction boiling at 18°-20°. A total of 32.4 g. (83% conversion) of $CF_3SCF=CF_2$ was obtained. Further distillation of the reaction mixture gave 22 g. of 95% pure $CF_3SCF_2CFCl_2$.

Anal. Calcd. for C_3F_6S: M.W. 182. Found: M.W. 180.

An infrared spectrum of pure $CF_3SCF=CF_2$ is shown in Figure A4 and the NMR analysis in Appendix B. A spectrum of 95% pure $CF_3SCF_2CFCl_2$ is shown in Figure A5.

d. Trifluorovinylsulfur Pentafluoride

SF_5Cl

Cesium fluoride (344 g., 2.26 moles), SF_4 (216 g., 2.0 moles) and chlorine (142 g., 2.0 moles) were reacted in a 1.5-liter autoclave according to a reported procedure.[14] The product mixture was washed by passing through two columns of water about 4 feet in length and 225 g. (69% conversion) of SF_5Cl obtained. GLC showed it to be 98% pure.

$CF_2ClCFHSF_5$[13]

A 12-liter flask was charged with SF_5Cl (31.1 g., 0.192 mole) and $CF_2=CFH$ (15.7 g., 0.192 mole) and irradiated with u.v. light for 10.5 hours. No liquid product was formed and infrared spectra of the overgas showed no evidence of reaction. Product was obtained by carrying out the reaction as described below.

A 300-ml. autoclave was charged with CCl_4 (15 ml.), benzoyl peroxide (0.6 g.), SF_5Cl (60.2 g., 0.37 mole), and $CF_2=CFH$ (37.1 g., 0.45 mole) and heated at 150° for six hours. The liquid product was distilled and 64.2 g. of material was obtained over the range 58°-61°. Analysis by GLC showed it to contain 82% SF_5CHFCF_2Cl (52.4 g., 0.215 mole). Conversion was 58%.

$CF_2=CFSF_5$[13]

Heptane (215 ml.) and SF_5CFHCF_2Cl (52.4 g., 0.215 mole) were placed in a 500-ml., 3-neck flask fitted with a stirrer, tube for addition of solid KOH, and a reflux condenser vented to a trap cooled to -186°. The solution was heated to reflux, and powdered KOH (38.5 g., 0.69 mole) was added in small amounts. A white solid was trapped in the -186° trap.

This material was distilled and an infrared spectrum of the product boiling at 15°-18° showed it to be $SF_5CF=CF_2$ (20.3 g., 0.098 mole) of 80% purity by GLC.

e. 2-Chloro-1-nitroso-1,2,2-trifluoroethyl Trifluoromethyl Sulfide

Two preparations were carried out as follows. A 1-liter Vycor flask was charged with $CF_3SCF=CF_2$ (2.64 g., 0.02 mole) and ClNO (1.31 g., 0.02 mole) and placed in sunlight for several hours. At the end of this time it contained a blue liquid and a blue overgas. This product was separated by GLC using an 8-inch column packed with Kel-F Acid 8114 ethyl ester and pure $CF_3SCF(NO)CF_2Cl$ (0.4 g., 0.0016 mole) was obtained. An infrared spectrum of this material is shown in Figure A7 and the NMR analysis in Appendix B.

f. Attempted Synthesis of Carboxysulfur Pentafluoride

$SF_5CH_2CH_2Cl$

A 12-liter flask fitted with a Vycor immersion well was evacuated and charged with SF_5Cl (60.3 g., 0.371 mole) and $CH_2=CH_2$ (7.70 g., 0.275 mole). The mixture was irradiated for six hours and then removed and distilled, giving 32 g. (61% conversion) of $SF_5CH_2CH_2Cl$.

$SF_5CH=CH_2$

A 300-ml., 3-neck flask was fitted with an addition funnel, stirrer, and reflux condenser vented to a trap cooled to -78°. Potassium hydroxide (18.0 g., 0.321 mole) was placed in the flask and H_2O (20 ml.) was added. As soon as the KOH dissolved, C_2H_5OH (60 ml.) was added. The solution was heated to reflux and $SF_5CH_2CH_2Cl$ (32.0 g., 0.168 mole) was added from the addition funnel. The mixture was refluxed for one hour and distilled giving 5.5 g. (21% conversion) of $SF_5CH=CH_2$, b.p. 38°-43°.

SF_5COOH

By oxidation of $SF_5CH=CH_2$: Vinylsulfur pentafluoride (1.35 g., 8.1 mmoles) was placed in a 3-neck, 100-ml. flask fitted with a stirrer, reflux condenser, and addition funnel containing a solution of $KMnO_4$ (2.5 g., 16 mmoles) in acetone (33 ml.) and H_2O (12 ml.). The $KMnO_4$ solution was slowly dropped into the reaction pot and MnO_2 formed almost immediately. After stirring for several hours the MnO_2 was filtered off, and the filtrate was acidified with H_2SO_4. A white solid formed immediately. This solid was filtered off and an infrared spectrum was made, but it did not show the presence of an S-F group. The filtrate was extracted with ethyl ether and an infrared spectrum made of the extracts, but it did not show S-F absorption.

By reaction of carbonyl fluoride with sulfur tetrafluoride: Two attempts were made to react SF_4 with COF_2 using CH_3CN as a solvent and one with tetramethylene sulfone as a solvent. The results of all three reactions were similar. One of them is described below.

A 300-ml. autoclave was charged with CsF (3.5 g., 0.023 mole), CH_3CN (50 ml.), SF_4 (28.0 g., 0.26 mole), and COF_2 (17.0 g., 0.26 mole) and heated at 200° for eight hours. The volatile products were removed and examined by infrared spectra. There was no evidence for the presence of any compound containing an S-F group. When the autoclave was opened it was found to be partially filled with carbonaceous material. It appears that reaction occurred with solvent.

By reaction of SF_5Cl with butyl lithium and carbon dioxide: A solution of butyl lithium (3.5 g., 55 mmoles) in hexane (~1.7 molar) was placed in a small 4-neck flask fitted with a stirrer, gas inlet, gas outlet, and low temperature thermometer. The reaction flask was cooled to -78° and SF_5Cl (8.72 g., 54 mmoles) was bubbled in at a rate so that the temperature did not rise above -55°. After the SF_5Cl was added, CO_2 (0.2 mole) was bubbled in at the rate of 80 cc/min. The solution was then allowed to warm to room temperature with continued carbonation. The solution was poured into 100 ml. of 6N HCl and a 2-layer mixture resulted. The hexane was evaporated and a layer of H_2O over a small amount of orange liquid was left. This liquid was separated and dried and an infrared and nuclear magnetic resonance spectrum were made. Neither spectrum showed evidence for SF_5. The water layer was extracted with ethyl ether; the extract was dried and an infrared spectrum made, but it showed no SF_5 absorption. The remainder of the water layer was then neutralized with NaOH. A solid was filtered off, but again it showed no evidence for the presence of a sulfur-fluorine compound.

g. Attempted Synthesis of SF_5NO

Reaction of disulfur decafluoride and nitric oxide at 150°

An 80-ml. Fischer-Porter tube was charged with S_2F_{10}* (2.06 g., 8.1 mmoles) and NO (0.486 g., 16.2 mmoles) and heated at 150° for three hours. During the reaction the tube became etched. The volatiles were separated by VPC and identified as NO_2, SO_2F_2, SOF_2, SO_2, SF_5OSF_5, NO, and S_2F_{10}.

A 300-ml., stainless steel autoclave was charged with S_2F_{10} (2.80 g., 11 mmoles) and NO (0.66 g., 22 mmoles) and heated at 150° for two hours. An infrared spectrum of the overgas showed N_2O, SOF_2, SO_2F_2, and SF_4. It was then heated for an additional 24 hours. Another infrared spectrum showed that SF_4 had disappeared and that the major product was SOF_2. There was no absorption to indicate the presence of SF_5NO.

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*Sample donated by Dr. James W. Dale, Monsanto Research Corporation.

Reaction of disulfur decafluoride and nitric oxide in electric discharge tube

A 1-liter flask was charged with S_2F_{10} (2.80 g., 11 mmoles) and NO (0.66 g., 22 mmoles) and connected to an electric discharge apparatus (Fig. 1) powered by a 15 kv, 30 mamp. transformer. A pressure of 5-7 mm was maintained during reaction. The products were caught at -196° and later separated by VPC. They were identified by infrared spectra as CF_4; CF_3Cl; SiF_4; N_2O; SF_6; SOF_2; SF_5Cl; SO_2; $SF_4(SO_3F)_2$; and an unknown with infrared absorption at 6.8, 8.12, 12.10, and 15.65 microns. The major product was SO_2. The CF_4, CF_3Cl, and SF_5Cl probably resulted from reaction with Kel-F grease used on the joints of the discharge apparatus. A small amount of sulfur was deposited in the discharge tube.

A 1-liter flask was charged with S_2F_{10} (2.80 g., 11 mmoles) and NO (0.66 g., 22 mmoles) and connected to the electric discharge apparatus powered by a 7.5 kv, 15 mamp. transformer. A pressure of 2-3 mm was maintained during reaction. A stream of air from an air gun was directed across the discharge tube during reaction, but it still warmed above room temperature. One-half of the material was reacted under these conditions, and the products were caught at -196°. These products were separated by VPC, and infrared analysis showed them to be CF_4, CF_3Cl; ClC(O)F; SiF_4; SF_6; N_2O; SO_2; S_2F_{10}; unknown with infrared absorption at 6.8, 8.12, 12.10, and 15.65 microns; and unknown with strong absorption at 8.61 and 9.06 and very strong absorption around 11.0 and 11.7 microns.

One-half of the material was reacted with the discharge tube cooled to -78°. These products were caught at -196° and separated by VPC. Infrared analysis showed them to be SiF_4; SF_6; N_2O; SO_2F_2; SOF_2; SO_2; S_2F_{10}; and an unknown showing absorption at 6.8, 8.12, 12.10, and 15.65 microns.

Reaction of sulfur tetrafluoride and nitrosyl fluoride

A 2075-ml. nickel reactor was evacuated and charged with sulfur tetrafluoride (250 mm., 3.0 g., 0.0277 mole) and nitrosyl fluoride (500 mm, 2.7 g., 0.0554 mole). The reactor was heated at 300° for two hours with little apparent reaction as determined by infrared analysis. Additional heating for two hours at 400°, however, resulted in a reaction. Infrared analysis showed the presence of SOF_2. Gas chromatographic separation of the product mixture on a Chromosorb-Kel-F 8114 ester column gave six peaks identified (in order of elution) as NO, SF_6, N_2O, SO_2F_2, SOF_2 and NO_2-SO_2.

Sulfur tetrafluoride (5.8 g., 0.054 mole) was condensed into a trap at -78°. Nitrosyl fluoride (5.5 g., 0.112 mole) was condensed into this yellow liquid, resulting in a green solution which was separated by warming to -40° to remove unreacted FNO. The higher boilers were washed free of SF_4 by bubbling through water. Infrared analysis of the products showed the presence of N_2O, SOF_2, NO_2, and SF_5Cl. Chlorine may have been introduced into the system either by Kel-F grease or by reaction with the NaCl windows of the infrared cell.

Reaction of nitrosyl chloride and SF_4Cs

A 300-ml flask containing a mixture of CsF (~3.8 g., 0.025 mole) and $CsSF_5$ (~6.6 g., .025 mole) was charged with NOCl (1.67 g., 0.025 mole), and the contents stirred. The volatile products were removed to a trap in liquid air and later separated by GLC They were identified by infrared spectra as ClNO, NO_2, SiF_4, SOF_2, SO_2F_2, SF_4, and SF_3Cl. There was no evidence for the formation of SF_5NO.

Reaction of sulfur tetrafluoride, cesium fluoride, and dinitrogen trioxide

Two reactions of CsF, SF_4, and N_2O_3 were carried out as described below.

A 1.4-liter autoclave was charged with SF_4 (23.5 g., 0.218 mole), CsF (34.4 g., 0.226 mole), and N_2O_3 (20.7 g., 0.272 mole) and heated at 100° for one hour, 150° for one hour, and 175° for two hours. The only product isolated other than starting material was SOF_2.

A 75-ml. monel cylinder was charged with SF_4 (4.32 g., 0.04 mole), and CsF (6.08 g., 0.04 mole) and heated at 150° for five hours. The cylinder was then charged with N_2O_3 (3.04 g., 0.04 mole)and placed in an ice bath. The cylinder was allowed to warm to room temperature over the weekend and the volatile products were analyzed The only products other than starting material were SOF_2 and a trace of SO_2F_2.

Reaction of SF_5Cl and nitric oxide

A 300-ml. autoclave was charged with SF_5Cl (1.86 g., 0.0115 mole), NO (0.345 g., 0.0115 mole), and benzoyl peroxide (0.3 g.) and heated at 100° for three hours. An infrared spectrum of the overgas showed that the only product formed was a small amount of SOF_2

Reaction of disulfur decafluoride and nitrosyl chloride

A 1-liter flask was charged with DMF (20 ml.), $AlCl_3$ (1.0 g.), S_2F_{10} (2.92 g., 0.0115 mole), and ClNO (0.75 g., 0.0115 mole), and the mixture was stirred for 0.5 hour at room temperature. An orange solution over a yellow solid developed. An infrared spectrum of the overgas showed only unreacted starting material. The reaction vessel was placed in a 70-85° bath for two hours with no further change.

h. Attempted Synthesis of Trifluoromethyl Thionitrite

Reaction of CF_3SAg and nitrosyl chloride

An 80-ml. Fischer-Porter tube was charged with CF_3SAg (1.00 g., 4.78 mmoles) dissolved in 1.0 ml. of dimethylformamide and ClNO (0.244 g., 3.76 mmoles). Nitrosyl chloride was charged into the tube by freezing it in liquid air, evacuating, and condensing from a tared flask.

After the tube was sealed it was allowed to warm to room temperature, but before it had warmed completely a reaction took place. The mixture was allowed to stand overnight at room temperature before an infrared spectrum was made of the overgas. It showed only CF_3SSCF_3. A white solid, probably AgCl, was also produced.

Reaction of bis(trifluoromethyl) disulfide and nitric oxide

Bis(trifluoromethyl) disulfide and nitric oxide were reacted using both u.v. light and electric discharge. Three attempts were made to prepare CF_3SNO by reaction of CF_3SSCF_3 with NO in the presence of u.v. light. The following is a typical reaction.

A 300-ml. quartz flask was charged with CF_3SSCF_3 (0.354 g., 1.7 mmoles) and NO (0.105 g., 3.5 mmoles) and irradiated with u.v. light from a Hanovia utility lamp, Type 30620, for 32 hours. The following compounds were found to be present in the indicated ratios (by gas chromatogram):

Compound	Relative Ratio	Compound	Relative Ratio	Compound	Relative Ratio
NO	190	Unknown	5	SO_2	470
CF_3NO	630	CF_3SCF_3	40	CS_2	330
N_2O	110	CF_3NO_2	30	CF_2SSCF_2	470

It is very likely that the CS_2 was originally present in the CF_3SSCF_3 as an impurity.

The reaction produced CF_3NO (1.3 mmoles) in 38% conversion. This amount represents 90% of the material formed from CF_3SSCF_3.

A small amount of CF_3SSCF_3 was placed in the bottom of the electric discharge tube which was cooled to -78°. A 1-liter flask charged with 500 mm. of NO was connected to the apparatus, and NO was passed over the CF_3SSCF_3 while a discharge was produced by a 15 kv, 30 mamp. transformer. The volatile products were trapped in liquid air and later separated by VPC. A small amount of very viscous material, insufficient for analysis, was left in the discharge tube. Infrared spectra of the volatiles showed them to be CF_2Cl; ClFC=O; CF_3SCl; NOCl; NO; NO_2; CF_4; N_2O; SO_2F_2; SOF_2; CF_3NO_2; SO_2; CF_3SSCF_3; unknown with absorption at 6.8, 8.12, 12.10, and 15.65 microns; and an unknown eluted from the VPC column about 45 minutes after CF_3SSCF_3 with absorption at 8.1, 8.3(s), 9.0(s) and 13.1 microns.

Reaction with trifluoromethanesulfenyl chloride and nitric oxide

Two reactions of CF_3SCl with NO were run. In the first reaction a 1-liter Vycor 7910 flask was charged with CF_3SCl (1.46 g., 10.7 mmoles) and purified NO (0.32 g., 10.7 mmoles). The materials were frozen into the flask as a white solid, allowed to warm to room temperature, and

irradiated with ultraviolet light for 16 hours. An infrared spectrum of the product mixture showed NO_2, SO_2, CF_3SCl, CF_2NO, CF_2NO_2, and SiF_4. An attempt was made to separate the mixture by GLC, but unsatisfactory resolution was obtained.

In the second reaction a 1-liter flask was charged with purified NO (0.642 g., 0.021 mole) by freezing it in as a white solid. As soon as the CF_3SCl (1.46 g., 0.011 mole) was condensed in, the solid material became bright red. On warming above the freezing point the color disappeared, but when the sample was solidified again the bright red color returned. Infrared spectra of the gas phase showed only starting materials. The reactants were transferred to a flask containing absolute ethanol and cooled in an attempt to develop the red color in a liquid phase. However, no color developed even when the alcohol was cooled to its freezing point. An infrared spectrum still showed CF_2SCl and NO.

Reaction of trifluoromethanesulfenyl chloride and nitrosyl chloride

Two reactions of CF_3SCl with NOCl were run. The following is a description of one reaction.

A magnetic stirring bar and several ml. of Hg were placed in a 1-liter flask which was then evacuated. This flask was charged with CF_3SCl (1.18 g., 0.009 mole) and NOCl (1.71 g., 0.026 mole), immersed in ice-water, and the contents stirred for three hours. The volatile products were removed to a trap in liquid air and later separated by a co-distillation. Some of the products were identified by infrared spectra as NO_2, ClNO, SiF_4, CF_3SCl, CF_3Cl, COF_2, and CF_3NO_2. In addition to these products there was a continuous elution of material which gave absorption in the CF region and in the NO_2 region, evidence that sample decomposition was occurring.

Reaction of bis(trifluoromethyl) disulfide and nitrosyl chloride

Three reactions of CF_3SSCF_3 with NOCl were run. The following is a description of one of them.

A 1-liter Vycor 7910 flask was charged with CF_3SSCF_3 (2.16 g., 0.011 mole) and ClNO (0.53 g , 0.011 mole) and placed in sunlight for four hours. As soon as the flask was placed in sunlight the brown color of the ClNO began to fade. At the end of four hours the flask was filled with a light yellow gas and covered with a thin, white, solid coating. The volatile products were separated by GLC and identified by their infrared spectra as ClNO, CF_3SSCF_3, NO, NO_2, SO_2, CF_3SCl, CF_3Cl, CF_3NO, CF_3NO_2, and an unknown eluted after CF_3SSCF_3.

Reaction of thiocarbonyl fluoride and nitrosyl fluoride

Nitrosyl fluoride (1 g.) was condensed into a Pyrex Fischer-Porter tube containing about 1 g. of impure thiocarbonyl fluoride. The tube was allowed to warm and an infrared spectrum was made of the overgas, which was found to contain SiF_4, COS and N_2O. Absorption between 8 and 9.2 microns and at 13.1 microns indicated a CF_2S group. Other unassigned peaks occurred at 6.15, 6.25, and 6.52 microns. The latter peak is probably due to CS, while the first two peaks may be due to NO. The spectrum changed over a period of time, indicating decompositon of the sample at room temperature.

1. Attempted Synthesis of Pentafluorophenyl Thionitrite

An 80-ml. Fischer-Porter tube was charged with pentafluorothiophenol (8.0 g., 0.040 mole) and sealed. The contents were frozen in liquid nitrogen, the tube was evacuated, and nitrosyl chloride (2.8 g., 0.043 mole) condensed in. The tube was placed in a -40° bath where it liquified and then rapidly solidified. The tube was warmed to room temperature. An infrared spectrum of the overgas showed NO, ClNO, SiF_4, and HCl. The overgas was pumped off and the solid (8.0 g.) was washed with benzene and dried. It was identified as $C_6F_5SSC_6F_5$, m.p. 49.5°-51° (rptd. m.p. 50-51°), m.wt. (f.p. in benzene) 388 (calcd. 398.2). Conversion was 100%. An infrared spectrum is shown in Figure A8.

J. Attempted Synthesis of 2-Chloro-1-Nitroso-1,2,2-trifluoroethylsulfur Pentafluoride

Trifluorovinylsulfur pentafluoride was reacted with nitrosyl chloride in both the gas phase and in solution as described below.

A 1-liter Vycor flask was charged with $SF_5CF=CF_2$ (2.39 g., 0.0115 mole) and ClNO (0.75 g., 0.0115 mole) and placed in sunlight. After about one hour the gas began to turn green. An infrared spectrum of the mixture at this point showed absorption at 6.2 microns in addition to new peaks in the C-F region. The flask remained in sunlight over the weekend. At this time there was a light green liquid present, but no colored overgas. An infrared spectrum showed only very weak absorption in the 6-6.5 micron region.

An 80-ml. tube was charged with dimethyl formamide (8.0 g.), $AlCl_3$ (1.0 g.), $SF_5CF=CF_2$ (2.08 g., 0.01 mole), and ClNO (0.65 g., 0.01 mole). As soon as the tube warmed to room temperature, a green solution with a blue overgas developed. After standing for about one hour the mixture developed into a blue gas over a two-phase liquid (green over blue). The blue overgas was trapped in another container and the bottom layer of blue liquid boiled out with it. The product was purified by GLC and identified by its infrared spectrum as $CF_2ClCFClNO$. No evidence was found for the presence of $SF_5CF(NO)CF_2Cl$.

k. Attempted Synthesis of 2-Chloro-2-Nitroso-1,1,2-Trifluoroethyl Trifluoromethyl Sulfide

A 1-liter Vycor flask was charged with CF_3SCF_2CFClI (4.50 g., 0.013 mole) and NO (0.51 g., 0.017 mole) and placed in sunlight for four days. At the beginning of the reaction the liquid reactant was almost colorless. It continuously turned a darker red and iodine began depositing on the walls of the flask. An infrared spectrum of the overgas showed absorption in the -NO region, 6.2 microns, as well as the C=F region 8-9 microns. It appeared that the major reaction was the decomposition of the starting material.

2. Synthesis of Fluoroaromatic Compounds

a. Pentafluoronitrosobenzene [32]

A solution of 90% H_2O_2 (100 ml.) and 90% HCOOH (400 ml.) in CH_2Cl_2 (2 l.) was placed in a 5-liter, 3-neck flask fitted with addition funnel, stirrer, and ice-water-cooled condenser. A solution of $C_6F_5NH_2$ (102 g., 0.55 mole) in CH_2Cl_2 (500 ml.) was rapidly added dropwise to the stirred solution. Shortly after addition was begun, the solution turned blue, then deep blue-green. Heating to reflux was begun and after about five minutes the solution was brown. In 15 minutes the color was green-brown and after 30 minutes the solution was again green. Refluxing was continued for five hours and the solution was then washed with six 500-ml. portions of water. The organic layer was dried over anhydrous magnesium sulfate and the solvent stripped until a pot temperature of 77° was reached. The remaining liquid was then distilled on an 18-inch spinning band column giving 48.8 g. of product, b.p. 51°/20mm. The pot residue, presumably $C_6F_5NO_2$, weighed 40.5 g. Recrystallization from pentane (2 ml./g.) gave 39.9 g. of product, m.p. 42°-44°. The compound may also be purified by sublimation.

b. Attempted Preparation of p-Nitrosotetrafluorobenzoic Acid

Tetrafluoroterephthalic acid (10 g., 0.042 mole) and water (500 ml.) were placed in a flask and heated to 60° while Ag C (4.98 g., 0.021 mole) was added in small amounts as it appeared to react. After about two hours the solution was evaporated to half its volume and then cooled. Some solid formed and was filtered off. The filtrate was washed with acetone and more precipitate formed and was filtered off. These filter cakes were recrystalized twice by dissolving in hot water and precipitating in excess acetone. The final product was a white solid which was oven dried and found to weigh 7 g. Analysis gave 32% Ag. Theory for $HO_2CC_6F_4CO_2Ag$ is 31.3% Ag.

Several grams of the silver salt were placed in an ampoule and shaken at room temperature with excess ClNO. When the ClNO was removed, a yellow solid remained. This solid was heated at 200° under complete vacuum with almost no noticeable change. An attempt was then made to isolate the product from the AgCl which was formed during its preparation by dissolving it in ethyl ether. However, the ether appeared to be wet as the product immediately turned white and gave off a gas which infrared showed to be NO. An infrared spectrum of the solid residue showed it to be tetrafluoroterephthalic acid.

c. p-Aminotetrafluoronitrosobenzene

Methylene chloride (175 ml.), 90% H_2O_2 (20 ml.) and 90% HCO_2H (70 ml.) were placed in a flask fitted with a stirrer, reflux condenser, and addition funnel containing p-$NH_2C_6F_4NH_2$ (9 g., 0.05 mole) in CH_2Cl_2 (200 ml.). This solution was added dropwise while the reaction mixture was heated to reflux. The solution turned orange-brown and remained that color during the five-hour refluxing. The mixture was washed with water and dried over Na_2SO_4. It was then transferred to a sublimation apparatus and the solvent removed under vacuum. After the solvent was removed, the solid was heated at 100° under total vacuum, and a green solid deposited on the cold finger (0.4 g.). Left in the sublimation apparatus was 4 g. of a red-brown solid which had an odor similar to $C_6F_4NO_2$. An infrared spectrum of the product is shown in Figure A12.

d. Attempted Synthesis of 4,4'-Dinitrosooctafluorobiphenyl

A solution of 4,4'-diaminooctafluorobiphenyl (23.5 g., 0.07 mole) in CH_2Cl_2 (600 ml.) was added rapidly to a stirred solution of 90% formic acid (100 ml.), 90% hydrogen peroxide (25 ml.), and CH_2Cl_2 (500 ml.). After initial formation of a deep blue-green color, the color faded to reddish-brown. After two hours at reflux a green color reappeared. Reflux was continued for five hours. The yellow-green solution was washed with six 500-ml. portions of water and dried over $MgSO_4$. The solution was stripped of solvent to a volume of about 100 ml. On cooling, 15.1 g. of yellow solid precipitated. The melting point of the sample depends on age, purity, and temperature at which the sample is placed in the melting point apparatus. The true melting point appears to be between 175°-185°. A second run using only 1 g. of the amine gave identical results.

3. Synthesis of Nitroso Esters and Derivatives

a. Synthesis of $CH_3O_2C(CF_2)_2CO_2NO$

The nitrite was prepared by two methods - reaction of $CH_3O_2C(CF_2)_2CO_2Ag$ with nitrosyl chloride and reaction of perfluorosuccinic anhydride with methyl nitrite. The latter method is described here.

Methyl nitrite (12.2 g., 0.2 mole) and perfluorosuccinic anhydride (34.2 g., 0.2 mole) were condensed into a Fischer-Porter aerosol compatibility tube and allowed to warm to room temperature. The tube was shaken to insure thorough mixing and soon became warm. After about 1-2 hours the tube had cooled and contained an amber liquid. Unreacted starting material was removed at reduced pressure. Yield was nearly quantitative.

Anal.: Calcd. for $C_5H_3F_4NO_5$: %C, 25.76; %H, 1.29; %F, 32.60. Found: %C, 25.84; %H, 1.33; %F, 45.25, 36.91.

An infrared spectrum of this compound is shown in Figure A14 and the NMR analysis in Appendix B.

b. Synthesis of $CH_3O_2C(CF_2)_3CO_2NO$

Methyl nitrite (12.2 g., 0.2 mole) and perfluoroglutaric anhydride (44.4 g., 0.2 mole) were reacted as described above with similar results.

Anal.: Calcd for $C_6H_3F_6NO_5$: %C, 25.44; %H, 1.06; %F, 40.28. Found: %C, 25.70; %H, 1.28; %F, 40.53.

An infrared spectrum of this compound is shown in Figure A15 and the NMR analysis in Appendix B.

c. Synthesis of $CH_3O_2C(CF_2)_2NO$

A 250-ml., 2-neck flask was fitted with an addition funnel containing $CH_3O_2C(CF_2)_2COONO$ (52 g., 0.223 mole) and a 15-inch Vigreaux column which was fitted with an air-cooled condenser constructed on the order of a Dean-Stark apparatus. The condenser was vented to a vacuum system through a -183° trap, and a total vacuum was maintained thoughout the system as the nitrite was dropped into the flask which was heated to 200°. The Vigreaux column was heated to 250°. After the pyrolysis had been going for several minutes, a blue product collected in the -183° trap and a colorless liquid began to condense in the air-cooled condenser. This liquid was periodically removed. The -183° trap was allowed to warm to room temperature and the remaining liquid product was washed with water. The blue product was separated and distilled twice by distilling from one trap to another under vacuum, discarding the last several ml. of liquid each time. A GLC of the final product (8.3 g., 20% conversion) showed it to be 100% pure.

Anal. Calcd for C H F NO: %C, 25.40; %H, 1.60; %F, 40.21. Found: %C, 25.66; %H, 1.72; %F, 40.42.

An infrared spectrum of this compound is shown in Figure A16 and the NMR analysis in Appendix B

d. Synthesis of CH O C CF NO

By pyrolytic decarboxylation

A 250-ml. 2-neck flask was fitted with an addition funnel containing CH O C CF COONO (33.0 g., 0.116 mole) and a 15-inch Vigreaux column vented to a vacuum system through a trap cooled to -183°. A complete vacuum was maintained throughout the system as the nitrite was dropped into the flask which was heated to 200°. The column was heated to 250. After the pyrolysis was completed, the material in the -183° trap was allowed to warm to room temperature, the nitrogen oxides were removed under vacuum, and the blue, liquid residue was washed with water. The blue product was separated and distilled twice by boiling from one trap to another under vacuum, discarding the last several ml. of liquid each time. A GLC of the final product showed it to be 100% pure. A total of 13 g of pure CH O C CF NO was obtained. Conversion was 47%.

Anal.: Calcd. for C H F NO: %C, 25.11; %H, 1.25; %F, 47.70. Found: %C, 25.30; %H, 1.17; %F, 47.40.

By photolytic decarboxylation

4-Carbomethoxyperfluorobutyryl nitrite (40 g., 0.14 mole) was placed in a 1-liter flask equipped with a Vycor immersion well and an outlet connected to a vacuum system through a trap cooled in liquid air. The nitrite was irradiated by a No. 8A36 Hanovia lamp suspended in the immersion well. Irradiation was continued for 48 hours at 0.1 mm pressure. The blue liquid product was removed from the trap and combined with the product from a similar experiment using 33 g. of nitrite. The combined products were fractionated to give 12 g. (20% conversion) of pure methyl 4-nitrosoperfluorobutyrate, b.p. 24°-26°/26 mm.

An infrared spectrum of this compound is shown in Figure A17 and the NMR analysis in Appendix B

e. Isolation of $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$

High-boiling liquid by-products from the preparation of $CH_3O_2C(CF_2)_3NO$ were combined and fractionated using a 24-inch glass helix packed column. The major portion of this material was removed at 137°-140°/0.1 mm. Infrared (Figure A18) and NMR analysis (Appendix B) were consistent with the structure $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$.

Anal.: Calcd. for $C_{15}H_9F_{18}NO_7$: %C, 27.45; %H, 1.37; %F, 52.00; %N, 2.13. Found: %C, 27.80; %H, 1.60; %F, 52.98; %N, 2.40.

f. Synthesis of $[H_2NOC(CF_2)_3]_2NO(CF_2)_3CONH_2$

Ethyl ether (150 ml.) and $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$ (113.5 g., 0.173 mole) were placed in a 250-ml. flask and cooled in ice-water. Ammonia was bubbled into the solution with rapid stirring until uptake of ammonia ceased. Ether was removed under vacuum and the residue was ground to a powder and dried in a vacuum oven at 50° to give 76 g. (72% conversion) of a white solid, m.p. 157°-160°. Infrared (Figure A20) and NMR analysis (Appendix B) were consistent with the structure $[H_2NOC(CF_2)_3]_2NO(CF_2)_3CONH_2$.

Anal.: Calcd. for $C_{12}H_6F_{18}N_4O_4$: %C, 23.50; %H, 0.98; %F, 55.90; %N, 9.15. Found: %C, 23.59; %H, 1.03; %F, 55.54; %N, 9.19.

g. Synthesis of $[NC(CF_2)_3]_2NO(CF_2)_3CN$

A 250-ml. flask containing thoroughly mixed P_2O_5 (150 g.) and the triamide (72.6 g., 0.119 mole) from the preceeding reaction was heated to 200° under vacuum. A liquid product distilled from the flask and was caught in a cold trap. Distillation gave 21.7 g. (33% conversion) of $[NC(CF_2)_3]_2NO(CF_2)_3CN$ boiling at 110°-115°/60 mm. Infrared (Figure A21) and NMR analysis (Appendix B) confirmed the assigned structure.

Anal.: Calcd for $C_{12}F_{18}N_4O$: %C, 25.82; %F, 61.28; %N, 10.04. Found: %C, 25.68; %F, 61.12; %N, 10.16.

h. Synthesis of $HO_2C(CF_2)_3NO$ by Hydrolysis of $CH_3O_2C(CF_2)_3NO$

Methyl 4-nitrosoperfluorobutyrate (10 g., 0.042 mole) was placed in an Erlenmeyer flask containing distilled water (60 ml.) and a magnetic stirring bar. The aqueous layer gradually acquired a blue color as the ester hydrolyzed. After five days the lower, organic layer was no longer present. The product, 4-nitrosoperfluorobutyric acid (7.0 g., 75% conversion), was isolated by salting out with sodium chloride.

i. Attempted Synthesis of $CH_2=CHCH_2O(CF_2)_3CO_2NO$

Allyl nitrite

Two syntheses of allyl nitrite were carried out. In the first synthesis no water was used, and although some allyl nitrite was prepared, the reaction mixture became badly charged. The following is a description of the second synthesis.

A 1-liter, 3-neck flask was fitted with a stirrer, a gas outlet vented through a trap cooled to -183° to a vacuum pump, and an addition funnel containing 130 ml. of 9M H_2SO_4. Into the flask were placed $CH_2=CHCH_2OH$ (116 g., 2 moles), $NaNO_2$ (175 g., 2.5 moles), and H_2O (100 ml.). The pressure was reduced to approximately 600 mm and the H_2SO_4 was added dropwise. After about 75% of the H_2SO_4 had been added, the mixture began giving off brown fumes and the reaction was stopped. The material caught in the -183° trap was distilled to give 175 ml. of a pale yellow liquid boiling at 47°. An infrared spectrum showed typical nitrite absorption.

$CH_2=CHCH_2O(CF_2)_3CO_2NO$

Two reactions were carried out. In the first reaction perfluoroglutaric anhydride (27 g., 0.12 mole) and allyl nitrite (11 g., 0.13 mole) were condensed into an 80-ml. tube at -183°. After it was sealed the tube was allowed to warm to room temperature. It detonated about 45 minutes after warming began.

In the second reaction anhydride (39 g., 0.170 mole) was placed in a 250-ml., 3-neck flask containing a stirring bar and fitted with a nitrogen inlet and outlet and an addition funnel containing allyl nitrite (22 g., 0.25 mole). The flask and its contents were maintained at 0° while the nitrite was added dropwise. After the addition was completed, the mixture was stirred for about one minute before a vigorous reaction took place, leaving a viscous, dark brown unidentified product.

j. Attempted Synthesis of $ClOC(CF_2)_3CO_2NO$

Three attempts were made to react perfluoroglutaric anhydride with ClNO to prepare $ClOC(CF_2)_3CO_2NO$. In the first reaction a 20-ml. ampoule was charged with anhydride (10 g., .05 mole) and ClNO (6.5 g., 0.10 mole) and allowed to stand at room temperature for two days. Removal of the more volatile material under vacuum left only the unreacted anhydride with no evidence for the formation of the nitrite.

In the second reaction a 1-liter, Vycor flask was charged with anhydride (6.6 g., 0.03 mole) and ClNO (0.27 g., .04 mole) and placed in sunlight. On warming to ambient temperature the liquid phase became red and the overgas was pale yellow. After several days the overgas acquired a slightly green color. Shortly after this the stopper popped from the flask and the contents were lost.

In the third reaction a 12-liter flask was charged with anhydride (30.0 g., 0.135 mole) and ClNO (8.0 g., 0.120 mole) and irradiated overnight with u.v. light through a Vycor immersion well. Before irradiation the pressure was 280 mm. The more volatile material was removed under vacuum and the highest boiling product was again found to be the anhydride.

4. Synthesis of Trifluoronitrosomethane and Other Nitrosoalkanes

a. Tritluoronitrosomethane

Trifluoroacetyl nitrite is added at a constant rate to a 5-liter flask containing refluxing FC-43 (3000 g.). The flask is fitted with a 2 x 24-inch column topped by a water-cooled condenser. The products are passed through the condenser to a wash column containing Raschig ring packing and circulating 7% aqueous NaOH, then through a $CaCl_2$ drying tube, a 2 x 40-cm. column containing Linde 4A Molecular Sieve, and finally into a trap immersed in liquid air.

In a typical run, 352 g. of CF_3NO was prepared from 945 g. of CF_3COONO, a conversion of 54%. About 120 g. of CF_3NO is prepared per day using this apparatus.

b. CF_2BrCF_2NO

A 72-liter flask was charged with $CF_2=CF_2$ (127 g., 1.27 moles) and BrNO (140 g., 1.27 moles) and irradiated with u.v. light for 24 hours. The mixture which was originally brown had now turned blue-green and was transferred to a flask for distillation. The mixture was distilled on a glass-packed column to give approximately 10 g. of CF_2BrNO boiling at 0° and 69 g. of CF_2BrCF_2NO boiling at 13°-20°. NMR analysis is given in Appendix B and an infrared spectrum is shown in Figure A23.

c. $CH_3OCFClCF_2NO$

Approximately 100 ml. of CF_2Cl_2 was condensed into a 300-ml. Fischer-Porter aerosol compatibility tube at -78° and stirred using a magnetic stirring bar. Nitrosyl chloride (7.5 g., 0.12 mole) was condensed into the tube and thoroughly mixed with the solvent. Methyl trifluoro-vinyl ether (10.5 g., 0.095 mole) was slowly condensed into the solution, with rapid color change occurring. Stirring was continued for two hours. The solvent was then evaporated from the tube on warming to room temperature. The tube was then connected through a trap in liquid oxygen to a vacuum system and evacuated. A total of 14.6 g. of blue liquid was collected. Trap to trap distillation gave 10.6 g. of $CH_3OCFClCF_2NO$, which was about 97% pure by GLC. The product was stored at 0°. NMR analysis is given in Appendix B and an infrared spectrum is shown in Figure A24.

d Attempted Synthesis of $ONCF_2CF_2CF_2NO$

A magnetic stirring bar, mercury (5 ml.), NO (0.10 g., 0.035 mole), and $I(CF_2)_2I$ (14.1 g., 0.035 mole) were placed in a 1-liter Vycor flask and the mixture was stirred in sunlight for eight hours. During this time a large amount of red solid deposited on the walls of the flask. The volatile material was removed to a trap in liquid air, forming a white solid with a trace of blue coloring. An infrared spectrum gave no evidence for normal nitroso absorption.

The reaction was repeated without the presence of Hg. The only difference in the product was that crystals of I_2 were deposited on the walls of the flask. There was still no evidence for the formation of a nitroso compound.

e. Attempted Synthesis of $CH_3OCF_2CF_2NO$

Tetrafluoroethylene (25 g., 0.25 mole) and methyl nitrite (13.7 g., 0.225 mole) were charged to a 12-liter flask equipped with a quartz immersion well. After u.v. irradiation for 48 hours with a No. 8A36 Hanovia lamp, trap to trap distillation gave mostly unreacted tetrafluoroethylene. A higher boiling blue product was also partially purified. Further purification of this product on VPC gave a pure sample. The compound was identified as $ONCF_2CF_2NO_2$ by NMR and infrared analysis.

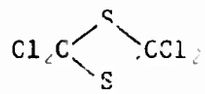
f. Reaction of Methyl Nitrite with Perfluorobutadiene

Methyl nitrite (1.2 g., 20 mmoles) and perfluorobutadiene (1.6 g , 10 mmoles) were charged to a 20-ml. ampoule. No reaction was apparent at room temperature in the absence of light. The ampoule was placed in sunlight for a total of 16 hours. A light green liquid resulted. After the unreacted material was removed, an infrared spectrum of the product indicated the reaction product was an unsaturated nitro compound.

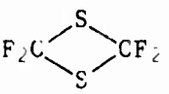
Methyl nitrite (1.2 g., 20 mmoles) and perfluorobutadiene (1.6 g., 10 mmoles) were charged to a 1-liter flask and irradiated with u.v. light from a Hanovia lamp type 8A36 for four hours. A light blue-green liquid was formed. Concentration of the blue liquid by trap to trap distillation gave only a trace of product, but the color quickly faded. The infrared spectrum was similar to the product obtained above.

5. Synthesis of Intermediates and Miscellaneous Compounds

a. Sulfur Containing Compounds

2,2,4,4-Tetrachlorodithietane[42] 

Thiophosgene (275 g., 2.4 moles) was placed in a dry, nitrogen-flushed 1-liter Vycor 7910 flask which was then fitted with an adapter and stopcock and placed in sunlight. After one day exposure the contents had solidified to the solid dimer. The flask was opened in the hood and 72 g. unreacted thiophosgene was decanted. The solid crystals were washed with hexane leaving 148 g. of the desired product. An additional 42 g. was recovered from the hexane wash.

2,2,4,4-Tetrafluorodithietane[43] 

Tetrachlorodithietane (108 g., 0.47 mole), antimony trifluoride (179 g., 1.00 mole), and tetramethylene sulfone (250 ml.) were placed in a 1-liter, 3-neck flask fitted with a stirrer and outlet to traps cooled to 0° and -183°. The mixture was heated with stirring to 90-100° and maintained at this temperature for one hour. The 0° trap was removed and the condensate (50.6 g.) distilled through a 70-cm. vacuum-jacketed column packed with glass helices. A cut (35.3 g.) boiling at 43-48° was obtained and washed until colorless with a solution of 10% NaOH (25 ml.) and 50% H_2O_2 (3 ml.). The organic layer was separated, dried over silica gel and refractionated to give 17.4 g. of product boiling at 48-48.3°.

Trifluoromethylthiosilver[44] CF_3SAg

A 300-ml. stainless steel autoclave was charged with AgF (14.88 g., 0.117 mole) and CS_2 (18.9 g., 0.248 mole) and heated at 140° for 12 hours. The volatiles were removed, and the remaining solid was extracted with dry acetone and filtered. A fine, brown suspension remained with the filtrate and could not be removed. The acetone was evaporated, and 5.5 g. of solid remained. An infrared spectrum of a Nujol mull of this solid showed absorption in the region 8.8-9.3 and 13.2-13.3 microns as reported for CF_3SAg.

Trifluoromethyliminosulfur difluoride $CF_3N{=}SF_2$

Sulfur tetrafluoride (70 g., 0.65 mole) and NaSCN (14 g., 0.17 mole) were reacted according to a reported procedure[45a] The products were separated by trap to trap distillation in a vacuum line. A portion of the product-rich fraction was subjected to preparative-scale chromatography using a 40-foot column packed with the ethyl ester of Kel F Acid 8114 on HMDS-treated Chromosorb to give 25 g. of pure $CF_3N{=}SF_2$.

Addition of sulfur chloride pentafluoride to 1,1-dichloro-2,2-difluoroethylene

i. Peroxide initiation

A 300-ml stainless steel autoclave was charged with SF_5Cl (18.92 g., 0.116 mole), $CF_2=CCl_2$ (12.33 g., 0.0927 mole), CCl_4 (15 ml.), and benzoyl peroxide (0.5 g.) and heated at 100° for 10 hours. Almost all of the starting material was recovered unreacted.

ii Ultraviolet initiation

The recovered reactants from the above reaction were placed in a 12-liter flask and irradiated with u.v. light over the weekend. Some liquid product was formed, and it was distilled on a spinning band column. One fraction was obtained at 106-114° (0.9 g.) and another at 114-115° (3.9 g.). Infrared spectra of these two fractions were identical.

In a second addition a 12 liter flask was charged with SF_5Cl (31.2 g., 0.192 mole) and $CF_2=CCl_2$ (25.5 g., 0.192 mole) and irradiated overnight with u.v. light. Distillation of the liquid product gave 5.58 g. of material boiling at 114-115°.

The reaction of equimolar amounts of SF_5Cl and $CF_2=CCl_2$ was repeated several times until about 60 g. of liquid product was obtained. This product was distilled on a spinning band column and a small amount of material was obtained at 100-104°. The material in the pot then appeared to undergo a reaction and vapors began passing through the condenser. An infrared spectrum of these vapors showed them to be SOF_2, SiF_4, and SF_6. The distillation pot was cooled to room temperature and the pressure reduced to 2 mm. At this pressure the major fraction (21 g.) boiled at 48-56°. An infrared spectrum of this material was similar to the spectrum of the proposed $SF_5CF_2CCl_3$, but not identical.

1,1,2,2-Tetrafluoroethyl methyl sulfide

A 12-liter Pyrex flask was fitted with a Vycor immersion well and inlet valve and evacuated. Methyl mercaptan (9.2 g., 0.192 mole), and tetrafluoroethylene (6.4 g., 0.064 mole) were bled into the flask and irradiated by an Hanovia type SOL lamp for four hours. The contents were then removed and partially purified by passing through traps at -8° and -133°. The contents of the -8° trap were distilled using an 18-inch spinning band column. A clear, colorless fraction (4.1 g.) was obtained boiling at 65-68° and identified as $CH_3SCF_2CF_2H$. Conversion was 42%.

b. Fluoroaromatic Compounds

Pentafluorophenyl hydrazine

Two separate reactions gave a total yield of 542 g. of $C_6F_5NHNH_2$. The following is a description of one reaction. Hexafluorobenzene (250 g., 1.34 moles) and hydrazine hydrate (141 g., 2.82 moles) were refluxed overnight with stirring in 600 ml. of tetrahydrofuran. About 500 ml. of solvent was stripped off, and the remaining hot solution was poured into 3 liters of H_2O. A pale yellow solid formed. This material was washed several times by stirring with water and decanting; finally, it was filtered, washed with water, and dried in a vacuum desiccator to yield 217 g. of pentafluorophenylhydrazine as a white powder (82% conversion).

1,2,4,5-Tetrafluorobenzene[45]

Three reactions were run. The following is a description of one of them.

A 5-liter flask was fitted with a stirrer, reflux condenser, and tubing for addition of solids. The flask was filled with 3200 ml. of 3N NaOH and the solution heated to reflux. Pentafluorophenylhydrazine (217 g., 1.1 moles) was added in small amounts over a one hour period. After the last addition the solution was refluxed an additional 2 1/2 hours. The mixture was distilled and a two phase product was obtained. The organic layer was separated and dried over $MgSO_4$. The water layer was extracted several times with xylene and these extracts were combined with the organic distillate over $MgSO_4$. After drying, the $MgSO_4$ was filtered off and the filtrate was distilled on a spinning band column. Fractions were taken as follows:

B.P. °C	n_D^{20}	Wt. g.
90-92	1.4088	55.4
92-93	1.4098	29.1
93-98	1.4149	16.7

Infrared spectra were the same for all fractions.

Tetrafluoroterephthalic acid[46]

A 3-liter, 5-neck flask was fitted with a stirrer, gas inlet, gas outlet, thermometer, and addition funnel and cooled to -78°. Butyl lithium (48 g. in 320 g. of hexane solution, 0.74 mole) was placed in the flask and cooled to below -70°. Tetrahydrofuran (1 liter) was cooled to -70° and poured into the BuLi. The addition funnel was filled with p-$C_6F_4H_2$ (55.4 g., 0.37 mole) in THF (75 ml.) and this solution was slowly dropped into the reaction mixture so that the temperature did not rise above -65°. The solution was stirred for two hours after the addition was

completed. The mixture was then carbonated by bubbling CO_2 through at a rate such that the temperature did not rise above -65°. At the end of three hours the flow rate was 180 l/hr. The mixture was allowed to warm to room temperature with continued carbonation. After it reached room temperature the mixture was poured into 1200 ml. of 6N HCl. The two phase mixture which developed was stripped of THF and about 600 ml. of water before a solid began dropping out. As the residue became thicker the distillation was stopped. The mixture was cooled in ice water and filtered. The filter cake was dissolved in hot water and decolorized with activated charcoal. This solution was filtered and cooled to 0°. The white solid which formed was filtered off and dried over P_2O_5 to give 72 g. (81% conversion) of tetrafluoroterephthalic acid, m.p. = 280-281°.

1,4-Dihydrazinotetrafluorobenzene[7]

Hexafluorobenzene (186 g., 1.0 mole), 95% hydrazine (141 g., 4.4 moles), and tetrahydrofuran (800 ml.) were stirred and refluxed for 45 hours. The mixture was cooled in ice and the precipitate removed by filtration. After washing with 500 ml. of water, 39 g. of crude 1,4-dihydrazinobenzene (m.p. 153-164°) remained. The remainder of the material (96 g.) was recovered from the THF solution, but consisted essentially of pentafluorophenylhydrazine and 1,3-dihydrazinobenzene as determined by infrared analysis.

An initial experiment on a 0.5 mole scale gave 17 g. of product.

1,4-Bis(acetophenone) tetrafluorophenyldihydrazone[8]

A solution of 1,4-dihydrazinotetrafluorobenzene (39 g., 0.22 mole), acetophenone (175 ml.), absolute ethanol (1500 ml.), and glacial acetic acid (15 ml.) was stirred at reflux for 16 hours. The solution was cooled in ice and the product (54.5 g., 69.8% conversion) separated by filtration. Recrystallization from isopropanol gave 50.5 g. of yellow plates, m.p. 160-162° (Rpt. 167.5-168°).

An initial experiment on a 0.1 mole scale gave 22 g. of product.

1,4-Diaminotetrafluorobenzene

1,4-Bis(acetophenone)tetrafluorophenyldihydrazone (45.0 g., 10.8 mmoles) was reacted with zinc (141 g., 2.16 moles) in acetic acid (860 ml.) at reflux temperature for 3 1/2 hours. The mixture was then filtered, washed with water (1250 ml.) and extracted with ether in a Soxhlet. The ether extract was labelled Sol. A. The water washings were combined with the original filtrate and extracted with benzene (five 375-ml. portions). This benzene extract was then washed with H_2O (five 250-ml. portions). After separation from H_2O the benzene extract was labelled Sol. B. The aqueous washings from Sol. B were neutralized with NaOH and extracted with ethyl ether. This ether extract was labelled Sol. C. Solutions A, B, and C were combined, dried over $MgSO_4$, filtered, and stripped of solvent. The dark red-brown residue was sublimed under vacuum at 120-130° to give 2.3 g. of a light tan solid. A melting point determination (95-120°) showed that the product was still impure.

1,2,4,5-Tetrafluorobenzene

Two reactions were run. The following is a description of one of them. A 500-ml., 3-neck flask was fitted with a stirrer, reflux condenser, and addition funnel and charged with 65% fuming H_2SO_4 (65.5 ml.), Br_2 (60.2 ml.), and $AlBr_3$ (2.2 g.). The addition funnel was filled with p-$C_6F_4H_2$ (43.0 g., 0.29 mole) which was slowly added to the solution in the flask. After the addition of $C_6F_4H_2$ was completed the solution was heated at 50-60° for four hours. The mixture was then poured over 4 liters of cracked ice. After the ice melted, the pale yellow precipitate which had formed was filtered off and washed several times with water followed by washings with Na_2CO_3 solution. The filter cake was then dissolved in methanol and precipitated by pouring into H_2O. The product (50 g.) was filtered and dried, m.p. 73-75°.

c. Nitroso Compound Precursors

1,2-Diiodotetrafluoroethane

The reaction was carried out twice in a similar manner with similar results. The following is a description of one reaction.

A 300-ml. autoclave was charged with C_2F_4 (45 g., 0.45 mole) and I_2 (127 g., 0.50 mole) and heated at 250° for 10 hours. A red liquid product was removed and washed with $Na_2S_2O_3$ until colorless. It was then dried over Na_2CO_3 and distilled to give a light pink liquid (96 g., 60% yield of CF_2ICF_2I) boiling at 67° at 166 mm. Hg.

1,3-Diiodohexafluoropropane

A 300-ml. autoclave was charged with perfluoroglutaryl chloride (100 g., 0.36 mole) and potassium iodide (130 g., 0.78 mole) and heated at 200° for 20 hours. A red liquid product was removed and washed several times with water. This was followed by washings with $Na_2S_2O_3$, then dilute NaOH, and finally several more washings with water. The product was then dried over Na_2SO_4 and distilled. This gave 52 g. (36% yield) of $ICF_2CF_2CF_2I$ boiling at 126-132°.

Attempted Synthesis of $(CH_3)_2NC(CF_2)_3COONO$ (O above C)

Perfluoroglutaric anhydride (22.2 g., 0.1 mole) and N-nitrosodimethylamine (7.4 g., 0.1 mole) were charged to a Fischer-Porter tube cooled to -183°. After melting had occurred the reactants were mixed thoroughly by shaking. The tube exploded soon after this latter step.

Preparation of CF_3SCF_2CFClI

A 12-liter flask was charged with CF_3SCl (34.3 g., 0.252 mole) and CF_2=CFI (24.2 g., 0.126 mole), and irradiated with u.v. light for three hours. During this time 22 g. of a red liquid was formed. This liquid was distilled on a spinning band column under reduced pressure (40 mm.). A large portion of the sample decomposed to give iodine. Two small fractions, both containing iodine, were obtained at 24-28° and 70-75°. Both fractions were washed with aqueous $Na_2S_2O_3$ to give colorless products; however, after the $Na_2S_2O_3$ solution was removed they both reverted to a deep red color. Nuclear magnetic resonance analysis of each sample gave inconclusive results. An infrared spectrum of the higher boiling material showed strong absorption at 8.48-8.68, 9.02, 9.32, 9.91, 12.61, and 14.30 microns, and weaker absorption at 11.52, 13.18, and 15.8-15.9 microns, indicating the presence of both CF_3S- and Cl-C groups. No further analyses were carried out because of its instability. The sample was reacted as soon as possible after isolation

d. Fluoroölefins

Tetrafluoroallene

i. $CF_2BrCH_2CF_2Br$[9]

Five similar preparations were carried out in a 1.4-liter autoclave. Another preparation on a larger scale was carried out in a 3-liter autoclave. The following is a description of a series of three preparations.

Dibromodifluoromethane (4.5 moles), 1,1-difluoroethylene (1.0 mole), and benzoyl peroxide (10.0 g.) were heated in a 1,4-liter stainless-steel rocking autoclave at 110° for five hours. CF_2Br_2 and CF_2=CH_2 were recovered by low-temperature distillation, leaving a residue containing the product, $CF_2BrCH_2CF_2Br$, and telomers of $CF_2Br(CH_2CF_2)_nBr$. After two additional runs utilizing recovered material, combination and distillation of the residue gave 270 g. of $CF_2BrCH_2CF_2Br$ (b.p. 72-75°/300 mm.) from a total of 132 g. of CH_2=CF_2 consumed (49.5% yield).

ii. CF_2BrCH=CF_2

Four preparations were carried out, the most successful being similar to a recent literature method.[50]

1,3-Dibromo-1,1,3,3-tetrafluoropropane (90 g., 0.33 mole) was added drop-wise to potassium hydroxide pellets (200 g.) in a 500-ml. flask fitted with a stainless-steel chain stirrer driven by a high torque motor. A nitrogen pressure of 300 to 350 mm. was maintained in the system with a slow sweep into traps at -78 and -196°. The flask was heated to 60°. As dehydrobromination occurred, the reaction mixture became dark and sticky.

Stirring became less efficient and the temperature rose to ~100°. Distillation of the contents of the cold traps gave 6% tetrafluoroallene (2.3 g., 0.02 mole) and 45% 3-bromo-1,1,3,3-tetrafluoropropene (30 g., 0.15 mole). The latter was further distilled through a small glass helix-packed column (b.p. 34°).

iii. $CF_2=C=CF_2$

Six reactions were carried out using a variety of different conditions. The results were poor. In some cases only a trace of product was obtained and identified by I.R. analysis. When powdered 90% potassium hydroxide was used at 100° the mixture became molten and no volatile products could be trapped. The following is a description of a more successful reaction.

In a 300-ml. flask fitted with an addition funnel and stainless-steel chain stirrer driven by a high torque motor, and connected to two traps at -183°, was placed 150 g. of pelleted potassium hydroxide. The flask was heated to 80° by a water bath while a slow stream of dry nitrogen was passed through the system. 3-Bromo-1,1,3,3-tetrafluoropropene (30 g., 0.15 moles) was added drop-wise. The low boiling product in the first trap was separated by a vaporization distillation and then purified by distillation on a low temperature still. Tetrafluoroallene (1.8 g., 0.15 moles) was obtained in 10% conversion (b.p. -38°).

Dehydrobromination of 275 g. of $CF_2BrCH_2CF_2Br$ in two steps by the method of Jacobs and Bauer[51] gave 24 g. of $CF_2=C=CF_2$. Conversion was 24% based on the starting alkane.

Methyl trifluorovinyl ether [52]

A total of 105 g. of $CH_3OCF=CF_2$ was prepared in two reactions. The following describes the larger reaction.

Dioxane (450 ml, dried over sodium, refluxed over and distilled from CaH_2), sodium methoxide (125 g., 98% commercial material), was charged to a 2180-ml. Monel cylinder fitted with a pressure gauge. α-Pinene (1 g.) was included to act as an inhibitor. Tetrafluoroethylene (180 g., 1.3 moles) was pressurized into the cylinder at ~270 psi. The reactor was placed in an autoclave rocker. A strong exotherm and pressure drop were noted 1 1/2 hours later. After 40 hours the low boiling products were stripped. Distillation on a low-temperature column gave 85 g. of material, b.p. 10-12.5°. VPC showed the product to be 95% pure.

4-Methyl-α,β,β-trifluorostyrene

4-Bromotoluene (10 g., 0.062 mole) was reacted with lithium in ether to form the lithium reagent. The solution was placed in a 300-ml. Fischer-Porter bottle and cooled in liquid nitrogen. The bottle was exhausted and excess tetrafluoroethylene was condensed into the bottle.

The bottle was sealed and placed in a cold bath at -30° for four hours. The mixture was hydrolyzed and the ether layer dried. Evaporation of solvent and vacuum distillation gave 4-methyl-α,β,β-trifluorostyrene (3 g., 30%), b.p. 90-92°/70 mm. n_d^{20} = 1.478. Reported b.p. 91.5°/70 mm, n_d^{20} = 1.481.

Attempted synthesis of perfluoroketene[53]

i. $ClCF_2\overset{O}{\overset{\|}{C}}Br$

Into a 3-neck flask fitted with a stirrer, thermometer, and reflux condenser were placed $CF_2ClCOOH$ (65.7 g., 50.1 mmoles), and PBr_5 (72.0 g., 16.7 mmoles). The mixture was stirred for one hour at room temperature and 3.5 hours at 70°. The mixture was then distilled on a glass-packed column and 68.9 g. of material was obtained, b.p. 46.5°. This represents a 71% conversion to $CF_2ClCOBr$.

ii. Reaction of $CF_2ClCOBr$ with Zinc

Two attempts were made to synthesize $CF_2=C=O$. No low-boiling product was obtained from either reaction. The following is a description of the second reaction.

Zinc (65.4 g., 1.0 mole) and 16 ml. of 6N HCl were stirred together in a 300-ml., 3-neck flask. The flask was then heated under vacuum overnight to remove excess HCl and H_2O. The flask was fitted with an addition funnel and a reflux condenser vented to a trap in liquid oxygen, and a solution of $CF_2ClCOBr$ (68.9 g., 35.9 mmoles) of ethyl ether was added. At first vigorous bubbling occurred, but this soon subsided. The flask was then heated with no apparent reaction taking place. Suddenly the contents of the flask began to undergo an apparent polymerization to produce a charred material which swelled out of the flask. No volatiles were caught in the -183° trap. Similar unsuccessful attempts to prepare this compound by this procedure were subsequently reported in the literature.[54,55]

Attempted synthesis of 1-trifluorovinyl perfluorocyclobutene

i. with $CF_2=CFLi$

Ethyl ether (75 ml.) and lithium (1.4 g., 0.2 mole) were placed in a small 3-neck flask fitted with a stirrer, gas outlet vented to a trap in liquid oxygen, and a gas inlet opening beneath the surface of the ether. Methyl bromide (12 g., 0.126 mole) was bubbled in at room temperature.

After this the flask was cooled to -78° and CF_2=CFBr (18 g., 0.11 mole) was bubbled in. This was followed by the addition of perfluorocyclobutene (17 g., 0.10 mole). The solution was allowed to warm to room temperature over the weekend. The only product obtained was a dark brown suspension of solids in the ether. Nothing in the product mixture contained the -CF=CF group as determined by infrared analysis.

ii. with CF_2=CFMgBr

Magnesium (4.8 g., 0.2 mole) and tetrahydrofuran (200 ml.) freshly distilled from $LiAlH_4$ were placed in a 500-ml. flask fitted with a stirrer, gas inlet, and low-temperature head vented to a trap in liquid oxygen. Throughout the reaction a stream of dry N_2 was passed through the mixture. The mixture was heated and CF_2=CFBr (32 g., 0.2 mole) was bubbled in until reaction began to take place; it was then cooled in ice while the remainder of the CF_2=CFBr was added. After this the perfluorocyclobutene (16 g., 0.1 mole) was bubbled in, and the mixture was allowed to warm to room temperature overnight. No volatiles were obtained. As before, the product was a suspended brown solid. All of the liquid was removed to another flask by vacuum and then distilled, but nothing other than starting material was obtained.

Preparation of $C_3F_7O[CF(CF_3)CF_2O]_2CF=CF_2$

$C_3F_7O[CF(CF_3)CF_2O]_2CFHCF_3$ (56.1 g., 0.1 mole) and dry ether (500 ml.) were placed in a 1-liter, 3-neck flask fitted with a stirrer and dropping funnel. Methyllithium (5% in ether, 55 ml., 0.11 mole) was added dropwise to the stirred solution. After addition was complete (~1 hour) the mixture was stirred for one hour. Methanol was added dropwise to destroy unreacted methyllithium and water was then added to dissolve the precipitated lithium fluoride. The ether layer was separated and the water layer extracted with ether. The ether layers were combined, dried over Na_2SO_4, and stripped under vacuum. The remaining crude product was distilled using a spinning band column. The major fraction (18.1 g.), b.p. 153.5-155°, was identified as the desired trifluorovinyl ether. The yield based on the single fraction was 33.5%.

Preparation of $C_3F_7O[CF(CF_3)CF_2O]_3CF=CF_2$ (A25)

The preceding reaction was repeated using $C_3F_7O[CF(CF_3)CF_2O]_2CFHCF_3$ (72.7 g., 0.1 mole) and methyllithium (0.1 mole). Crude material (65 g.) was distilled to give 45 g. of product boiling at 188°/45 mm. The infrared spectra of the two ethers were nearly identical.

e. Miscellaneous Compounds

Perfluoropropylene epoxide[56]

Water (150 ml.), KOH (84 g.), CH_3OH (1000 ml.), and 50% H_2O_2 (473 ml.) were stirred together in a flask and cooled to -60°. Liquid $CF_3CF=CF_2$ (105 g., 0.70 mole) was added and the mixture was stirred at -60° for two hours. It was then allowed to warm slowly to room temperature and the product (54.4 g.) was collected in a -78° trap. Analysis by VPC showed the product to be 80% perfluoropropylene epoxide with unreacted perfluoropropylene as the impurity. A small amount of this product mixture was shaken in an ampoule with excess Br_2. An infrared spectrum of the overgas showed pure epoxide.

Perfluoroglutaric anhydride

Perfluoroglutaryl chloride (910 g., 3.3 moles) was slowly added with stirring to 150 ml. water in a 3-liter flask. After the acid chloride had been added, the water was removed by azeotroping with benzene. The benzene was distilled off at atmospheric pressure, then by aspirator. Excess P_2O_5 was then mixed thoroughly with the perfluoroglutaric acid and heated. The anhydride was collected (600 g., 83%) directly by distillation.

Perfluorosuccinic anhydride

Perfluorosuccinic acid (200 g., 1.05 moles) was mixed with excess P_2O_5 in a 1-liter flask. The mixture was heated and perfluorosuccinic anhydride (141 g., 0.82 mole) was removed by distillation as formed.

Perfluoro(2-methyl-3,6-dihydro-1,2,2H-oxazine)

Trifluoronitrosomethane (4.3 g., 0.043 mole) and perfluorobutadiene (6.8 g., 0.043 mole) were condensed into a Fischer-Porter tube and kept at -25° for 72 hours. After this time the blue color of the nitroso compound had disappeared. The volatile material (~5 g.) was removed from the tube by vacuum distillation and found to consist essentially of $CF_3\underline{NCF_2CF=CFCF_2O}$. Yields on several runs averaged 50%. The following properties were observed: b.p. 51-52°, n_D^{20} 1.2789, d_4^{20} 1.6075.

Anal: Calcd for C_5F_9NO: %C, 23.01; %H, 0.00; %F, 65.52
Found: %C, 23.32; %H, 0.00; %F, 65.38.

Nitrosyl bromide

A 500-ml., 3-neck flask was fitted with a stirrer, a gas inlet tube, and an outlet tube vented to traps at -78° and -183°. Water (80 ml.) and $NaNO_2$ (383 g., 5.5 moles) were stirred in the flask as HBr was bubbled in. It appears that no reaction takes place until the HBr concentration reaches a certain point. The product was caught in the -78° trap and distilled on a glass-packed column to give 42 g. of material boiling at 8°.

It was found that the following is the better method of producing BrNO. A 1-liter flask containing 567 ml. of concentrated HBr solution (7 moles) was fitted with a stirrer, gas outlet vented to -78° and -183° traps, and an addition funnel containing 345 ml. of a solution of $NaNO_2$ (3 moles). The flask was maintained at ambient temperature with a water bath and the $NaNO_2$ solution was slowly added. The product was trapped at -78°.

Methyl nitrite

Methanol (32 g., 1 mole) was dissolved in an equal volume of water and added to a flask containing 70 g. $NaNO_2$. The mixture was stirred and concentrated H_2SO_4 slowly added. The evolved gas was passed through a $CaCl_2$ tube and collected in a trap cooled in liquid air. The product (57 g., 93%) was condensed into a cylinder and stored under refrigeration.

Monosodium hexafluoropentanediol

Hexafluoropentanediol (21.2 g., 0.10 mole) and sodium (1.15 g., 0.05 mole) in 200 ml. of dry ether were stirred by means of an air motor for 48 hours. Formation of a white solid occurred slowly. After filtering and drying under vacuum for six hours, 12 g. of $NaOCH_2CF_2CF_2CF_2CH_2OH$ was collected. Evaporation of ether solution yielded 9 g. of the unreacted diol.

Attempted preparation of disodium hexafluoropentanediol

Three attempts were made to obtain the disodium salt. In the first, hexafluoropentanediol (5 g.) was dissolved in 50 ml. dry ether and refluxed over sodium for one week. The white solid which precipitated was dried and analyzed by titration. Found: eq. wt. 225; 236 Theory for monosodium salt, 234; for disodium salt, 128.

Hexafluoropentanediol (5 g.) was dissolved in 50 ml. diglyme and heated with sodium overnight just below the boiling point. A black tar was obtained.

Attempted epoxidation of perfluorobutadiene

1. by H_2O_2

Water (150 ml.), KOH (84 g., 1.5 moles), and CH_3OH (1.1 liter) were placed in a 3-neck flask fitted with a gas inlet, stirrer, and addition funnel containing 45% H_2O_2 (480 ml.). When the KOH had dissolved the mixture was cooled to -40° and the H_2O_2 slowly added. The addition funnel was then replaced with a low-temperature (-78°) head and $CF_2=CF-CF=CF_2$ (50 g., 0.31 mole) was added through the gas inlet. This mixture was stirred for 2 1/2 hours at -40° and then allowed to warm to room temperature.

The volatiles were caught in a trap cooled to -183°. Only a small amount of material was caught and this proved to be mostly CO_2 with a trace of C_2F_6. Distillation of the reaction mixture which was found to have a pH ~5 gave only 1.8 g. of material boiling below the boiling point of methanol. This material was separated by GLC. Methanol, tetrafluoroethylene, and perfluorobutadiene were isolated as well as several unidentified compounds. Infrared spectra of these volatile compounds showed no peaks in the 6-7 micron region where a perfluorinated oxirane usually absorbs. NMR analysis indicated that one of the products was $CF_2CH{=}CFCF_2O$.

ii. by Oxygen

A 1-liter Vycor flask was charged with $CF_2{=}CFCF{=}CF_2$ (2.4 g., 0.015 mole) and O_2 (0.48 g., 0.015 mole) and placed in sunlight for five days. At the end of this time the flask contained a water-white liquid. An infrared spectrum of the overgas showed some unreacted diene and a peak at 6.6 microns (thought to be $-CF-CF_2$ with O bridging) as well as other peaks. A spectrum of the liquid also showed absorption at 6.5-6.6 microns.

The reaction was repeated on a larger scale. A 12-liter flask was charged with C_4F_6 (20.7 g., 0.128 mole) and O_2 (8.19 g., 0.256 mole) and irradiated with a u.v. lamp through a Vycor immersion well. After 24 hours an infrared spectrum of the vapor phase showed a peak at 6.6 microns and the reaction was stopped. Although the products were not isolated and identified, it appears that epoxidation can be effected by this method.

b Polymer Synthesis

Polymers were prepared using bulk, solution, and suspension techniques and are described in Tables 3-8

Bulk polymerizations were carried out in either glass ampoules (20-80 ml.) or mild steel cylinders (500 and 900 ml.), generally with agitation at the temperatures indicated. Solution polymerizations were carried out in sealed glass ampoules, while suspension polymerizations were carried out in glass ampoules, mild steel cylinders, and a stirred autoclave.

Liquid monomers were weighed and added to the tubes; gaseous monomers were expanded into an evacuated 1-liter flask at measured pressure and condensed into the polymerization tubes. The tubes were then placed in a cold bath for the indicated time. If a suspension polymerization was run, the tube was shaken vigorously The suspending medium was water containing 3 g LiBr and 3 5 g $MgCO_3$ per 100 ml In working up the products, the unreacted gases were vented and the volatile materials recovered by vacuum distillation. The polymer was then removed and weighed. In the case of suspension polymerizations, the mixture was first treated with concentrated HCl to remove the $MgCO_3$, and washed several times before vacuum drying

Polymers were frequently purified by dissolving in a suitable solvent such as Freon 113 and reprecipitating with methanol. They were then dried under vacuum.

In order to carry out these low temperature polymerizations, a system including a refrigerated bath and stirred reactor was constructed. The apparatus (shown in Fig. 2) consists of five components. The compressor (A) cools a reservoir (B) of $CaCl_2$ solution which is circulated by a pump (C) through a polymerization bath (D) and an autoclave (E).

(A) The compressor is a commercial unit, a 1.5 horse-power Copelametic, which uses R-502 as a refrigerant. The compressor is connected to two large copper coils sealed inside the reservoir.

(B) The reservoir is a tank 12 inches x 18 inches x 36 inches containing two cooling coils from the compressor bathed in the coolant which is circulated throughout the system. Near the bottom the reservoir has an outlet tube which leads to the pump and at the top an inlet tube for the return of the coolant. The reservoir is filled with 20 gallons of a 29 6% $CaCl_2$ solution which is gravity-fed to the pump and can be maintained at any temperature between ambient and -40° within 1.5°F. It is insulated on all sides with six inches of polystyrene and encased in a vapor sealed plywood box

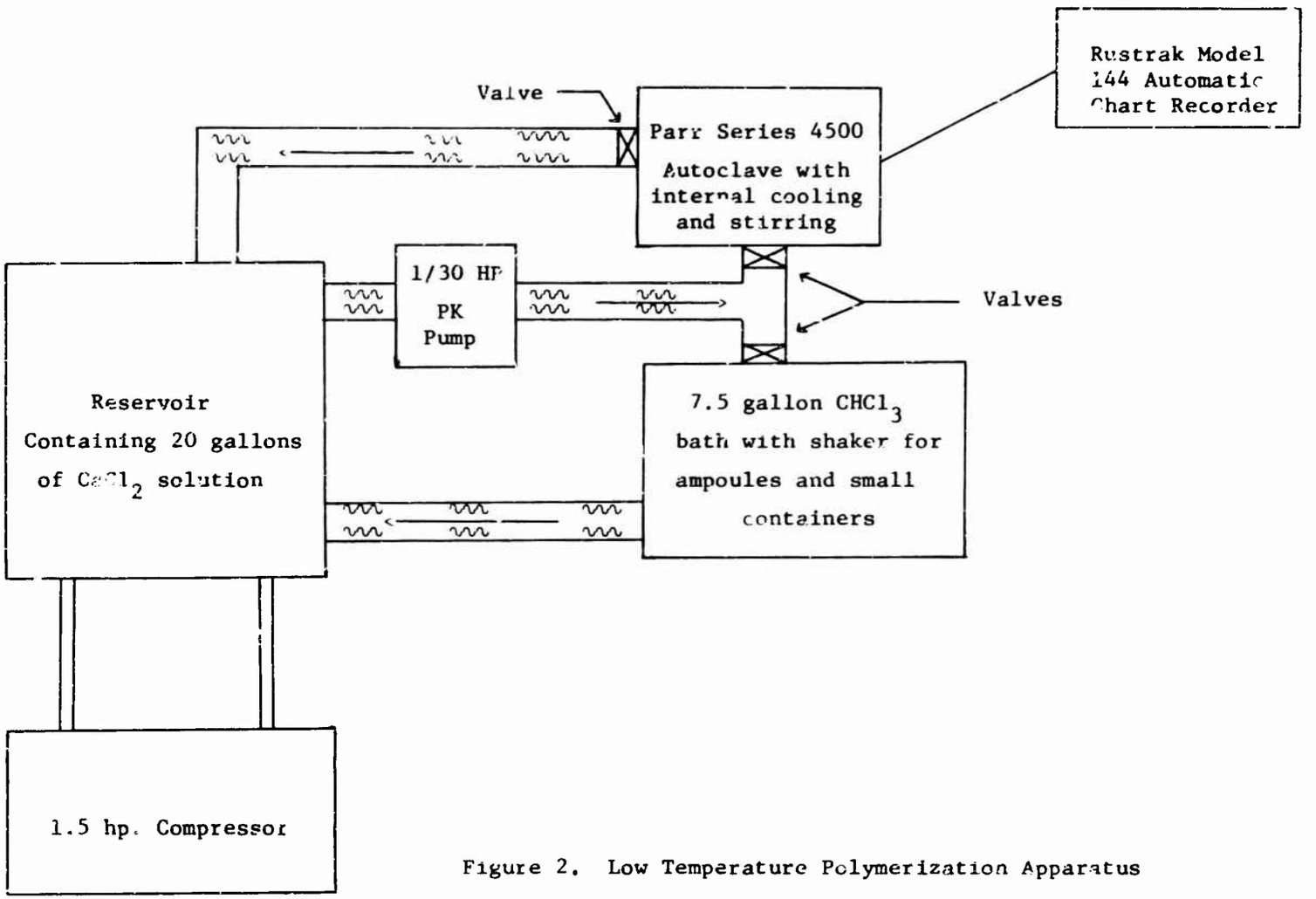


Figure 2. Low Temperature Polymerization Apparatus

(C) The first pump used in the system was an Oberdorfer centrifugal pump connected directly to a 3450 RPM motor, but it was found that this unit was transferring too much heat to the cooling system. The situation was remedied by adapting an ordinary pump used for circulating water in lab-scale distillations, a 1/30 horse-power PK pump. This pump was connected to the system through 5/8" copper tubing and then insulated with polyurethane foam. The pump is gravity-fed from the reservoir and forces the coolant through the polymerization bath and autoclave and then through the return inlet at the top of the reservoir

(D) The polymerization bath is a steel tank 12 inches x 18 inches x 18 inches surrounded by a water jacket 9 inches high and 1 1/2 inches wide. The CaCl solution from the reservoir is circulated through the jacket which is baffled so that the coolant must circulate completely around the tank which is filled with CHCl to a depth of six inches. Three inches from the top of the tank a 3/4 inch brass rod mounted in air-tight bearings at each wall extends the length of the tank and six inches beyond one end. This extended end of the shaft is connected by a rocker arm to a pin and bushing mounted off-center in a pully powered by a 1/18 horse-power Bodine motor The motor is controlled by a Variac to give the degree of agitation desired on the brass rod. Several wire baskets which hold the polymerization vessels are suspended from the brass rod into the CHCl bath. The entire tank is insulated with three inches of polyurethane and encased in a wooden box with a removable, insulated lid.

(E) The autoclave used is a 2000-ml., Parr Series 4500, stirred, pressure reaction vessel with an internal cooling coil. As received from the factory, the cooling coil was made of 1/4 inch O.D. stainless steel, but after the first run it was apparent that this coil was too small to provide sufficient cooling. It was, therefore, replaced first with a 1/4 inch O.D. copper coil (which also proved unsatisfactory) and finally a 3/8 inch O.D. stainless steel coil was used. The autoclave, stirring motor, and holder are encased in a plywood box insulated with five inches of polystyrene and a temperature of -30°C was easily obtained

The temperature on the autoclave is monitored with a Rustrak automatic chart temperature recorder, Model 144.

TABLE II

PROPERTIES OF NEW COMPOUNDS PREPARED

No.	Compound	I.R. Fig. No.	NMR Page No.	ELEMENTAL ANALYSIS Calculated %C	%H	%N	%F	Found %C	%H	%N	%F	b.p.°C/ mm.Hg	Remarks
1.	$CF_3SCF{=}CF_2$	A4	1									18-20	Mol. Wt. Calcd. = 182; Found = 180
2.	$CF_3SCF(NO)CF_2Cl$	A7	2										
3.	$CF_3NCF_2CF{=}CFCF_2O$		3	23.01			65.52	23.32			65.38	51-2	n_D^{20} = 1.2789
4.	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2\overset{O}{\overset{\|}{C}}ONO$	A14	4	25.76	1.28		32.60	25.84	1.33		36.91		
5.	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2\overset{O}{\overset{\|}{C}}ONO$	A15	5	25.44	1.06		40.28	25.70	1.28		40.53		
6.	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2NO$	A16	6										
7.	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	A17	7	25.11	1.25		47.70	25.30	1.17		47.40	24-6/26mm	
8.	$[CH_3O\overset{O}{\overset{\|}{C}}(CF_2)_3]_2NO(CF_2)_3\overset{O}{\overset{\|}{C}}OCH_3$	A18	8	27.45	1.37	2.13	52.00	27.80	1.60	2.40	52.98	137-40/ 0.1mm	
9.	$[H_2N\overset{O}{\overset{\|}{C}}(CF_2)_3]_2NO(CF_2)_3\overset{O}{\overset{\|}{C}}NH_2$	A20	9	23.50	0.98	9.15	55.90	23.59	1.03	9.19	55.54		m.p = 157-60°C
10.	$[NC(CF_2)_3]_2NO(CF_2)_3CN$	A21	10	25.82	0.00	10.04	61.28	25.68	0.24	10.16	61.12	110-113	
11.	$[CH_3O\overset{O}{\overset{\|}{C}}(CF_2)_2]_2NO(CF_2)_2\overset{O}{\overset{\|}{C}}OCH_3$	A19	22	28.40	1.78	2.76	45.00	28.52	1.99	3.98	45.03		

TABLE III

COPOLYMERS OF CF_3NO AND $CF_2=CF_2$

CF_3NO		C_2F_4			Time		Yield		
g.	mmoles	g.	mmoles	Reaction System	(hr.)	Temp(°C)	(g.)	% Conv.	Remarks
53.0	530	53.0	530	Bulk in 300-ml. autoclave	60	-30	60	57	Product is elastomeric gum
17.0	170	17.0	170	Suspension in Fischer-Porter tube	48	-30	20	58	Elastomeric gum
41.4	420	40.0	400	Bulk	240	-30			Fractionated to give 38 g. [n] = 0.44
50.4	510	50.5	510	Suspension in stirred autoclave	48	-30	30	30	Reactor leaked; only 10 g. of monomer recovered
94.0	950	95	950	Suspension in stirred autoclave	48	-25	99	53	Contained some insoluble material
53.5	540	54.0	540	Bulk in 500-ml. cylinder	22	-3[illegible]	82	76	[n] = 1.15 (in FC-43)

TABLE IV

COPOLYMERS OF CF_3NO WITH OTHER OLEFINS AND DIENES

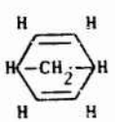
No.	CF_3NO g.	CF_3NO mmoles	Comonomer Structure	Comonomer g.	Comonomer mmoles	System	Time (hr.)	Temp(°C)	Yield (g.)	% Conv.	Remarks
1.	6.9	65	$CF_2=CFCF=CF_2$	10.8	65	Suspension	48	-20	5.2	34	Elastomeric gum
2.	4.3	43	"	6.8	43	Bulk	72	-25	4.1	36	Elastomeric gum
3.	30.7	310	"	50	310	Suspension	48	-35	22	27	Gum; [n]=0.1 in FC-75
4.	59	600	"	97.4	600	Bulk	41	-40	45	29	Gum: [n]=0.1 in FC-75; recovered 31.4 g. volatiles and 61.2 g. of $CF_3\overline{NCF_2CF=CFCF_2O}$
5.	2.1	21	$CF_2=CFCH_2CH=CH_2$	2.6	21	Suspension	48	-20	1.4	30	Brown, tacky gum
6.	2.97	30	$CF_2=C=CH_2$	2.28	30	Bulk	18	-20			Gum; decomposes at room temp.; evolves unidentified fluorine-containing gas
7.	0.99	10	$C_4H_9CF=CF_2$	1.3	10	Bulk	18/240	-25/ambient			Liquid product which reacted with glass container to produce SiF_4
8.	0.99	10		0.90	10	Bulk	18	-15			Product was orange liquid which decomposed to brown solid and etched glass container

TABLE IV (Cont'd)

COPOLYMERS OF CF_3NO WITH OTHER OLEFINS AND DIENES

No.	CF_3NO g.	CF_3NO mmoles	Comonomer Structure	Comonomer g.	Comonomer mmoles	System	Time (hr.)	Temp(°C)	Yield (g.)	% Conv.	Remarks
9.	3.5	35	CF_2=CFBr	5.8	35	Bulk	18	-78 to 25	8.2	89	Tough white gum; good elemental analysis for CF_3NO/CF_2=CFBr; Tg=3°; insol. in FC-43
10.	13.9	140	"	22.5	140	Bulk	18	-20	20	60	White, tough elastomer
11.	3.5	35	"	5.6	35	Bulk	4	-30	7.4	81	White, hard elastomer
12.	3.5	35	"	5.6	35	Bulk	2	Ambient			Fluid liquid
13.	4.3	43	CF_2=CFCl	5.0	43	Bulk	48	-30	7	75	Elastomeric gum
14.	5.0	50	CF_2=CFI	11.1	53	Bulk	15	-30			Dark, brown solid; iodine produced
15.	3.5	35	CF_3SCF=CF_2	6.4	35	Bulk	65	-30	2	20	Gum; Tg= -48°; [η]=0.068
16.	0.60	6	CH_3OCF=CF_2	0.67	6	Bulk	3	-78			Tough colorless gum; insoluble in $CF_2ClCFCl_2$

TABLE V

COPOLYMERS OF $CF_2=CF_2$ WITH OTHER NITROSO COMPOUNDS

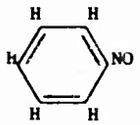
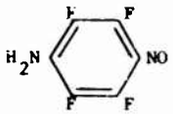
No.	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Comonomer Structure	Comonomer g.	Comonomer mmoles	System	Time (hr.)	Temp.(°C)	Yield (g.)	% Conv.	Remarks
1.	1.4	14		1.8	9	Solution in CH_2Cl_2	48	-20			0.28 g. soluble polymer and 1.70 g. insoluble white compound; for $C_6F_5NO/CF_2=CF_2$ Calcd: %C,32.3; %N,4.7; %F,57.55 Found: %C,32.2; %N,4.7; %F,57.55
2.	2.0	20		2.0	19	"	18	-35	3.07	77	Product was black powder which dissolved in acetone to give black solution
3.	2.2	22		0.30	15	"	14	-15			Tacky, yellow solid
4.	1.0	10	CF_2BrCF_2NO	2.1	10	Bulk	12	-78 to ambient	2.6	84	Elastomeric gum
5.	0.73	7.3	$CH_3OCF(NO)CF_2Cl$	1.30	7.3	Bulk	66	-35			Blue, sticky gum

TABLE VI

TERPOLYMERS

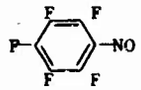
No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer Structure	Termonomer g.	Termonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
1.	0.89	9	1.0	10		0.20	1	Solution in CH_2Cl_2	24	-40	1.6	77	Tacky gum
2.	1.9	19	2.4	24	"	0.20	1	"	24	-30 to -20	3.35	75	
3.	2.88	30	5.0	50	"	3.96	20	Solution in $CF_2ClCFCl_2$	48	-30	10	84	Gum; fractionated; $[\eta]$ = 0.16
4.	0.99	10	0.90	9	$CF_3SCF=CF_2$	0.226	1.2	Bulk	48	-38			Viscous, pale-blue polymer; most of thioether recovered
5.	3.5	35	2.9	29	"	1.1	6	Bulk	65	-30			White gum
6.	0.29	2.9	0.36	3.6	$CF_3SCF(NO)CF_2Cl$	0.18	0.7	Bulk	18	-20			Viscous liquid; IR indicated CF_3NO/C_2F_4 only
7.	0.26	2.6	0.33	3.3	"	0.16	0.7	Bulk	42	-20			Tacky gum; IR and NMR indicate CF_3S- in polymer
8.	2.1	21	1.1	11	$CF_2=CFCF=CF_2$	1.7	11	Suspension	72	-20	2.3	47	Viscous, sticky liquid
9.	8.5	85	6.4	64	"	3.3	21	Suspension	48	-30	9.5	50	Elastomeric gum
10.	12.8	130	10.8	110	"	3.2	20	Bulk	48	-30	10	33	Gum; fractionated; $[\eta]$ = 0.36
11.	4.0	40	2.0	20	$CF_2=CFCF=CF_2$	3.2	20	Bulk	48	-35	6.1	66	Sticky gum; $[\eta]$=0.15
12.	4.4	44	2.2	22	$CF_2=CFCH=CH_2$	2.4	22	Suspension	20	-20	3.0	33	Viscous, sticky liquid
13.	6.9	69	3.2	32	"	3.5	32	Suspension		-20			Exploded after ~5 min.
14.	22	220	17	170	"	4.6	50	Suspension	48	-30	7.5	17	Elastomeric gum
15.	3.2	32	2.2	22	"	1.2	10	Bulk	72	-30	5.8	88	Clear, elastomeric gum

TABLE VI (Cont'd)

TERPOLYMERS

No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer Structure	Termonomer g.	Termonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
16.	12.8	130	10.8	110	"	2.1	20	Bulk	12	-30	10	39	Gum; fractionated; [n]=0.14
17.	8.0	80	4.0	40	"	4.3	40	Bulk		-78			Exploded
18.	6.0	60	3.0	30	"	3.5	30	Bulk		-78			Exploded
19.	49.5	500	40.0	400	"	11.0	100	Bulk	15	-35	40	40	White gum
20.	85.1	859	63.4	634	"	24.3	225	Suspension in stirred autoclave	64	-32	43.5	25	[n]=0.2
21.	99	1,000	80	800	$CF_2=CFCH=CH_2$	21.6	200	Bulk	17	-42	120	60	[n]=0.16 in FC-75
22.	13.9	140	12	120	$CF_2=CFBr$	3.9	24	Bulk	48	-30	21	70	Elastomeric gum; [n] = 0.36
23.	13.9	140	9.5	95	"	7.6	47	Bulk	48	-30	19	61	Elastomeric gum; [n] = 0.10
24.	13.9	140	7.0	70	$CF_2=CFBr$	11.3	70	Bulk	48	-30	28	90	Elastomeric gum; [n] = 0.11
25.	3.5	35	2.9	29	"	0.9	6	Bulk	12	-78 to 25	6.7	92	9.4 mole % $CF_2=CFBr$ in polymer; Tg= -45°; [n] = 0.155
26.	3.5	35	2.3	23	"	1.9	12	Bulk	12	-78 to 25	6.5	84	21.7 mole % $CF_2=CFBr$ in polymer; Tg= -35°; [n] = 0.135
27.	3.5	35	1.7	17	"	2.8	17	Bulk	12	-78 to 25	7.1	89	31 mole % $CF_2=CFBr$ in polymer: Tg= -21°
28.	25 0	250	14.0	140	"	19.8	120	Bulk	48	-30	42	71	White gum

TABLE VI (Cont'd)

TERPOLYMERS

No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer Structure	Termonomer g.	Termonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
29.	16.6	170	17.1	171	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2NO$	3.8	20	Bulk	48	-30	25	66	Gum; fractionated; [η] = 0.32
30.	16.6	170	17.1	171	"	2.0	10	Bulk	48	-30	15	42	Gum; fractionated; [η] = 0.36
31.	18.9	191	21.2	212	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	5.5	21	Bulk	24	-32	22.5	50	[η] = 0.26
32.	16.7	169	21.2	212	"	10.1	42	Bulk	24	-32	21.0	44	[η] = 0.29
33.	77.1	779	94.5	945	"	37.4	156	Bulk	24	-30	168	80	[η] = 0.50
34.	356	3,600	400	4,000	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	95.5	400	Bulk		-45			Exploded after several hours; recovered 145 g. polymer; [η] = 0.25 in FC-75
35.	125.8	1,271	154	1,540	"	60.8	255	Bulk in 3 reaction vessels	36	-30	245	72	10 g. unreacted nitroso ester recovered
36.	20.0	200	22.5	225	$HO\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	5.6	25	Bulk	18	-35	16.5	34	Colorless gum
37.	1.9	19	1.5	15	$CH_3OCF=CF_2$	0.34	3	Bulk	18	-35	2.2	60	Elastomeric gum; IR shows C-H; only partially soluble in FC-43 at 75° after 5 days
38.	9.9	100	8.0	80	"	2.24	20	Bulk	48	-35	19	95	Gum; [η] = 0.64
39.	34.0	344	27.5	275	"	7.7	69	Bulk	42	-35	62.5	90	Gum; could not be cured with benzoyl peroxide at 120° for 15 hr.
40.	5.58	56.4	7.05	70.5	$CH_3OCFClCF_2NO$	2.50	14.1	Bulk	42	-35	14	93	Gum; IR shows C-H; [η] = 0.28

TABLE VI (Cont'd)

TERPOLYMERS

No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer Structure	Termonomer g.	Termonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
41.	1.6	16	1.9	19	$CF_2=CFCF_2NO$	0.4	2	Bulk	108	-35	2.7	69	Colorless gum; IR of fractionated polymer shows $CF_2=CF-$
42.	2.5	25	1.25	12.5	$CF_2=C=CF_2$	1.40	12.5	Bulk	69	-32	2.6	50	Low mol. wt. oil
43.	4.0	40	2.0	20	"	2.24	20	Bulk	69	-30	4.9	59	Gum; fractionated; [n]=0.13; Tg= -35°
44.	43.0	430	21.6	220	"	24.0	220	Bulk	72	-30	30	34	White gum; IR shows $CF_2=$
45.	3.96	40	2.0	20	$CF_2=C=CH_2$	1.52	20	Bulk	120	-20 to ambient	6.3	84	Decomposes at 70°
46.	2.10	21	1.10	11	$CF_2=CFCH_2CH=CH_2$	1.30	11	Suspension	48	-20	1.5	33	Brown, viscous liquid
47.	6.0	60	3.0	30	"	3.7	30	Bulk	18	-38			Brown, low mol.wt. fluid
48.	1.10	11	0.80	8	$(CF_2=CFCF_2CFCl-)_2$	1.80	3	Suspension	24	-20	0.7	17	Viscous liquid
49.	3.8	38	2.7	27	$(CF_2=CFCF_2)_2CFCl$	3.2	11	Bulk	48	-30	5	52	Viscous liquid; some diene incorporated
50.	3.1	31	2.5	25	$(CF_2=CFCH_2CF_2-)_2$	1.8	6	Bulk	48	-35	4.5	61	White gum (appears to be cross-linked); IR shows $CF_2=CH-$
51.	2.5	25	2.8	28	$CF_2ClCF(NO)CH_2CH=CH_2$	0.5	2	Bulk	114	-38	2.0	35	Viscous brown polymer; IR shows $CH_2=CH-$
52.	0.50	5	0.56	5	$F_2C=S$	0.41	5	CF_2Cl_2 sol. of $(C_2H_5)_3B$ and O_2	180	-10			Brown gum

TABLE VI (Cont'd)

TERPOLYMERS

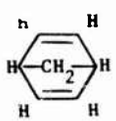
No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer Structure	Termonomer g.	Termonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
53.	2.20	22	2.20	22	CF_3OF	0.45	4.3	Bulk	18	-25	3	62	Tacky gum
54.	2.10	21	1.10	11	$C_2H_5OCH=CH_2$	0.78	11	Bulk	144	-20	2	50	Clear, viscous liquid
55.	2.20	22	1.10	11	$CH_2=CHOCH_2CH_2OCH_2CH=CH_2$	1.40	11	Bulk	14	-78	2.4	52	Brown gum
56.	4.3	43	3.7	37	$CH_2=CHCH=CH_2$	0.3	5	Bulk	48	-30	7	88	Viscous liquid; decomposes rapidly in air
57.	4.0	40	2.5	25	$CH_2=C(CH_3)_2CH=CH_2$	1.8	25	Bulk		0			Exploded
58.	3.0	30	3.0	30	"	0.68	10	Bulk		0			Exploded
59.	3.0	30	2.0	20	"	0.68	10	Bulk	24	-78	3	53	Tacky gum; turns brown
60.	4.95	50	4.0	40		0.92	10	Bulk	72	-35			Viscous, yellow liquid product decomposed to brown tar at room temp.

TABLE VII

MISCELLANEOUS POLYMERS

No.	Monomer	g.	mmoles	System	Time(hr.)	Temp.(C°)	Yield (g.)	% Conv.	Remarks
1.		1.00	5	Solution in CH_2Cl_2	24/72	-40/-20	1.3	81	Pale yellow solid; for C_6F_5NO/CF_2=CFCl; Calcd: %C, 30.6; %N, 4.46; %Cl, 11.3; %F, 48.5; Found: %C,30.3; %N, 4.46; %Cl, 13.7; %F, 45.4
	CF_2=CFCl	0.59	5						
2.	CF_3NO	2.2	22	Bulk		-25			Exploded after 5 minutes
	CF_2=CFCF=CF_2	1.8	11						
	CF_2=CFCH=CH_2	1.2	11						
3.	CF_3NO	3.2	32	Bulk	18	-25	5		Tacky gum
	C_2F_4	2.2	22						
	CF_2=CFCF=CF_2	0.83	5						
	CF_2=CFCH=CH_2	0.58	5						
4.	CF_3NO	1.8	18	Bulk	48	-25	0.8		Tacky gum
	CF_3CF=CF_2	1.4	9						
	$CF_3\overline{CFCF_2O}$	1.5	9						
5.	F_2C=S	0.82	10	Bulk	72/72/72	-78/-30/25	Trace		Small amount of $\{CF_2S\}_x$ formed
	$CF_3\overline{CFCF_2O}$	1.66	10						

TABLE VII (Cont'd)

MISCELLANEOUS POLYMERS

No.	Monomer	g.	mmoles	System	Time(hr.)	Temp.(C°)	Yield (g.)	% Conv.	Remarks
6.	$CH_3OCF(Cl)CF_2NO$	1.70	9.6	Bulk	18	-78			Mixture of purple and white polymers; purple polymer reacted with CH_3OH to give the white product
	$CH_3OCF=CF_2$	1.08	9.6						
7.	$CF_3\overline{CFCF_2O}$	3.80	22.9	Bulk	312	85			Viscous liquid; reaction produced SiF_4; product slowly soluble in H_2O to give acidic solution
	$HOCH_2(CF_2)_3CH_2OH$	5.09	24.5						
8.	CF_3NO	0.37	3.8	Bulk	90	-35			Slightly viscous liquid
	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	0.9	3.8						
	$CF_2=CFCF=CF_2$	1.23	7.6						
9.	CF_3NO	0.50	5	Bulk	36	-35			Opaque gum; acid fumes evolved
	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	1.20	5						
	$CF_2=CFCH=CH_2$	1.08	10						

TABLE VIII

UNSUCCESSFUL POLYMERIZATIONS

	CF_3NO		$CF_2=CF_2$		Termonomer or Comonomer				Time	Temp.	Yield	%	
No.	g.	mmoles	g.	mmoles	Structure	g.	mmoles	System	(hr.)	(C°)	(g.)	Conv.	Remarks
1.	0.495	5			$SF_5CF=CF_2$	1.04	5	Bulk	168	-17			No reaction
2.	4.3	43			CHF=CHF	2.8	43	Bulk	720	-30			No reaction
3.	2.1	21			$CF_2CF=CFCF_2$	3.3	22	Bulk	72	-20			No reaction
4.	5.45	55			CF_3CFCF_2O	9.0	49	Activated charcoal	720	25-60			No reaction
5.	1.6	15			CH_2CH_2O	0.7	16	Bulk	96	-25			No reaction
6.	1.8	18			$CCl_2=CClCCl=CCl_2$	4.6	18	Bulk	72	Ambient			No reaction
7.	2.5	25			$F_2C=O$	1.7	25	Bulk in 5-ml nickel tube at 18,000 psi.	48	Ambient			No reaction
8.	1.1	11			$(CF_3)_2C=O$	1.8	11	"	5	Ambient			No reaction
9.	0.495	5			$F_2C=S$	0.41	5	In CF_2Cl_2 solution of $(C_2H_5)_3B$ and O_2	360/240	-10/ ambient			No copolymerization
10.	1.1	11			SO_2	0.7	11	Bulk	96	-2[illegible]			No reaction
11.	1.0	10			$(CN)_2C=C(CN)_2$	1.4	10	Bulk	96	Ambient			No reaction
12.	0.12	1.2			$(CF_3)_2C=S$	0.22	1.2	Bulk	360	-78			No reaction
13.			1.0	10	$CH_3\overset{ON\ O}{N-C}-C_6H_4-\overset{O\ NO}{C}-NCH_3$	2.5	10	Solution in acetone	120	25			No reaction
14.			4.1	41	$(CH_3)_2NNO$	3.0	41	Bulk	336	-20 to ambient			No reaction
15.			1.7	17	CH_3ONO	1.04	17	Bulk	42	Ambient			No reaction
16.			0.50	5	$(C_2H_5)_3B$	0.41	5	CF_2Cl_2 solution of $(C_2H_5)_3$ and O_2	18	-10			No copolymerization

TABLE VIII (Cont'd)

UNSUCCESSFUL POLYMERIZATIONS

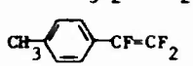
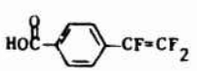
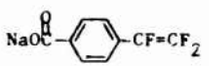
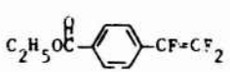
No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer or Comonomer Structure	g.	mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
17.			1.2	12	$Cl_2C=S$	1.3	11	Bulk	24/432	-38/Ambient			No reaction
18.			0.1	1	$(CF_3)_2C=S$	0.19	1	Bulk	168	-78			No reaction
19.	0.24	2.4	0.24	2.4	$SF_5CF=CF_2$	0.50	2.4	Bulk	48	-17			No SF_5- incorporated in polymer
20.	4.8	48	4.3	43	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF=CF_2$	1.0	5	Bulk	48	-30	7	77	Elastomeric gum; no ester incorporated
21.	5.4	54	4.3	43	$CF_3CH_2OCF_2CF=CF_2$	0.70	3	Bulk	48	-30	7	68	Tacky gum; no ether incorporated
22.	2.2	22	1.1	11	$C_2H_5OSi(CH_3)_2CF=CF_2$	2.5	11	Bulk	240	-35	3.1	53	Clear liquid; no silane incorporated
23.	2.2	22	1.1	11	$ClSi(CH_3)_2CF=CF_2$	1.8	11	Bulk	48	-25	2.0		"
24.	3.0	30	2.5	25		0.9	5	Bulk	48	-30	4	63	Viscous liquid; styrene incoporation inconclusive
25.	3.0	30	2.5	25		1.0	5	Solution in C_2H_5OH	48	-30	4	62	Viscous liquid; no acid incorporated
26.	3.0	30	2.5	25		1.0	5	Suspension	72	-30	4	62	Gum; no acid incorporated
27.	3.0	30	2.7	27		0.7	3	Bulk	48	-35	2.5	44	White gum; no ester incorporated

TABLE VIII (Cont'd)

UNSUCCESSFUL POLYMERIZATIONS

No.	CF_3NO g.	CF_3NO mmoles	$CF_2=CF_2$ g.	$CF_2=CF_2$ mmoles	Termonomer or Comonomer Structure	Termonomer or Comonomer g.	Termonomer or Comonomer mmoles	System	Time (hr.)	Temp. (C°)	Yield (g.)	% Conv.	Remarks
28.	2.1	21	1.1	11	$\overline{CF_2CF=CFCF_2}$	1.6	11	Bulk	72	-20	0.7	14	Viscous liquid; no C_4F_6 incorporated
29.	4.3	43	3.2	32	CFH=CFH	0.6	11	Bulk	96	-30	5	62	No CFH=CHF in polymer
30.	4.3	43	2.2	22	CH_2=CHCN	1.2	22	Bulk	72	-30			Viscous gum; no CH_2=CHCN incorporated
31.	2.2	22	1.1	11	$\overline{CH_2CH_2O}$	0.47	10	Bulk	96	-25	1.6	42	Tacky gum; no $\overline{CH_2CH_2O}$ incorporated
32.	1.1	11	0.54	5.4	SO_2	0.34	5.4	Bulk	96	-25	1.0		Tacky gum; no SO_2 incorporated
33.	4.4	44	2.2	22	$(CF_3)_2C=O$	3.6	22	Bulk	48	-30	3	30	Tacky gum; no ketone incorporated
34.	1.78	18	1.8	18	$CF_3\overline{CFCF_2O}$	2.99	18	Bulk	120	-35 to -10	3.15		100% of $CF_3\overline{CFCF_2O}$ recovered unreacted

TABLE IX

NMR ANALYSIS

(Peak areas in percent of total area)

Sample Solvent	78.4.2 Neat	78.5.2 Neat	83.1.2 Neat	78.6.2 Freon 113	78.7.1 Freon 11	78.8 Neat
Shift ppm (CF_3COOH)						
-20.0						1.6
-18.2	4.3				2.7	
-15.0	1.7					1.6
-12.0	21.1	46.1	44.0	41.7	39.4	44.4
-9.9	25.2	6.3	5.7		6.2	
-8.9					2.4	
-6.4	5.7	1.2	1.4		1.6	
Total CF_3	58.0	53.6	51.1	41.7	52.3	47.6
+9.6					1.4	
+11.4	10.9	20.6	22.8	25.8	19.5	22.6
+14.0	3.7	1.2	1.4	2.9	1.4	4.4
+21.5	7.7	5.5	5.7	4.4	4.9	4.0
+23.7	6.0	16.5	17.4	23.4	17.6	21.4
+26.3	2.3				0.8	
+27.1	5.4			1.6		
+28.2	6.0	2.3	1.4		2.2	
Total CF_2	42.0	46.1	48.7	58.1	57.8	52 4

Description of sample polymerization:

78.4.2 Bulk, 25°, 1:1 CF_3NO: $CF_2=CF_2$

78.5.2 Same as above

83.1.2 Terpolymer with CF_2Br_2, bulk, 25°, 1:1:1 monomer ratio

78.6.2 In Freon 113, -15° to 25°, 5:1 CF_3NO:$CF_2=CF_2$

78.7.1 In Freon 113, -15° to 25°, 1:5 CF_3NO:$CF_2=CF_2$

78.8 In cyclohexane, 25°, 1:1 CF_3NO:$CF_2=CF_2$, Ziegler catalyst

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NMR analysis and interpretation were carried out by Dr. Wallace Brey of the Department of Chemistry of the University of Florida. Many helpful ideas and suggestions during this program were contributed by Dr. Paul Tarrant and Dr. George Butler, consultants for Peninsular ChemResearch, Inc. Polymerizations using cobalt-60 as an irradiation source were carried out through the cooperation of Dr. Robert Hanrahan of the Department of Chemistry of the University of Florida.

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APPENDICES

APPENDIX A

Infrared Spectra

Figure

A1. 2,2,4,4-Tetrafluoro-1,3-dithietane

A2. Thiocarbonyl Fluoride

A3. Perfluorothioacetone

A4. Trifluoromethyl Trifluorovinyl Sulfide

A5. Trifluoromethyl 2,2-Dichloro-1,1,2-trifluoroethyl Sulfide

A6. Trifluorovinylsulfur Pentafluoride

A7. 2-Chloro-1-nitroso-1,2,2-trifluoroethyl Trifluoromethyl Sulfide

A8 Bis(pentafluorophenyl) Disulfide

A9 Pentafluoronitrosobenzene

A10. Pentafluorobenzoyl Nitrite

A11. Tetrafluoroterephthalyl Mononitrite

A12. p-Aminotetrafluoronitrosobenzene

A13. 4,4'-Diaminooctafluorobiphenyl Oxidation Product

A14 3-Carbomethoxyperfluoropropionyl Nitrite

A15 4-Carbomethoxyperfluorobutyryl Nitrite

A16. Methyl 3-Nitrosoperfluoropropionate

A17. Methyl 4-Nitrosoperfluorobutyrate

A18. $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$

A19 $[CH_3O_2C(CF_2)_2]_2NO(CF_2)_2CO_2CH_3$

A20. $[H_2NC(=O)(CF_2)_3]_2NO(CF_2)_3C(=O)NH_2$

A21 $[NC(CF_2)_3]_2NO(CF_2)_3CN$

A22. 4-Nitrosoperfluorobutyric Acid

A23. 1-Bromo-1,1,2,2-tetrafluoro-2-nitrosoethane

A24. Methyl 1-Chloro-1,2,2-trifluoro-2-nitrosoethyl Ether

A25. $C_3F_7O[CF(CF_3)CF_2O]_3CF=CF_2$

A26. $CF_3NO/CF_3SCF=CF_2$ Copolymer

A27. $CF_3NO/CF_2=CFBr$ Copolymer

A28. $CF_3NO/CF_2=CF_2/C_6F_5NO$ Terpolymer

A29. $CF_3NO/CF_2=CF_2/CF_2=CFCF=CF_2$ Terpolymer

Figure

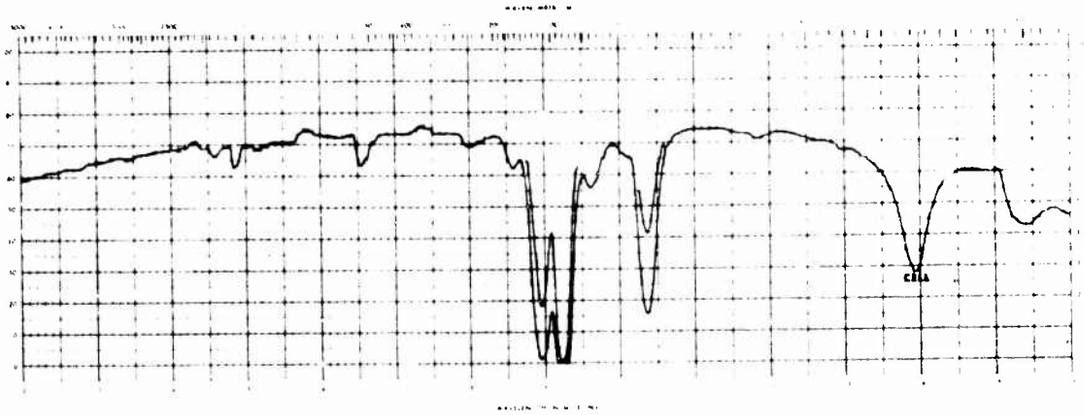


Fig. A1. 2,2,4,4-Tetrafluoro-1,3-dithietane
(gas, 4 and 8 mm)

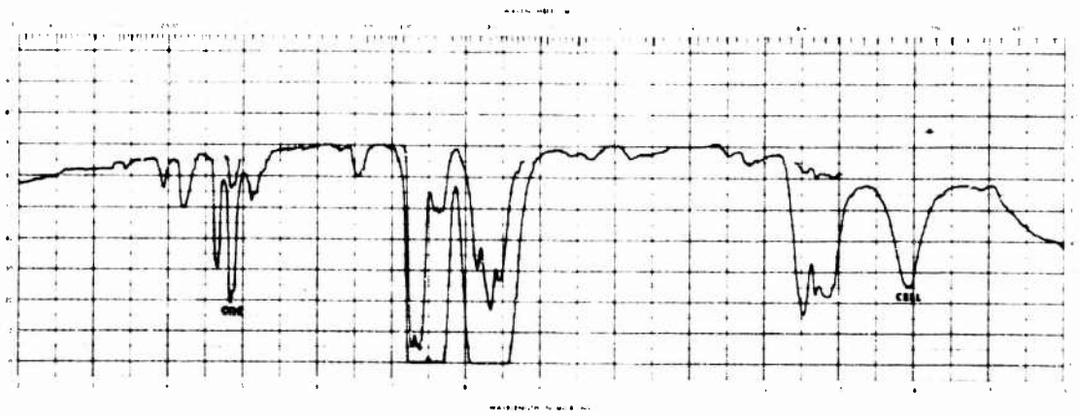


Fig. A2. Thiocarbonyl Fluoride
(gas, 6 and 90 mm)

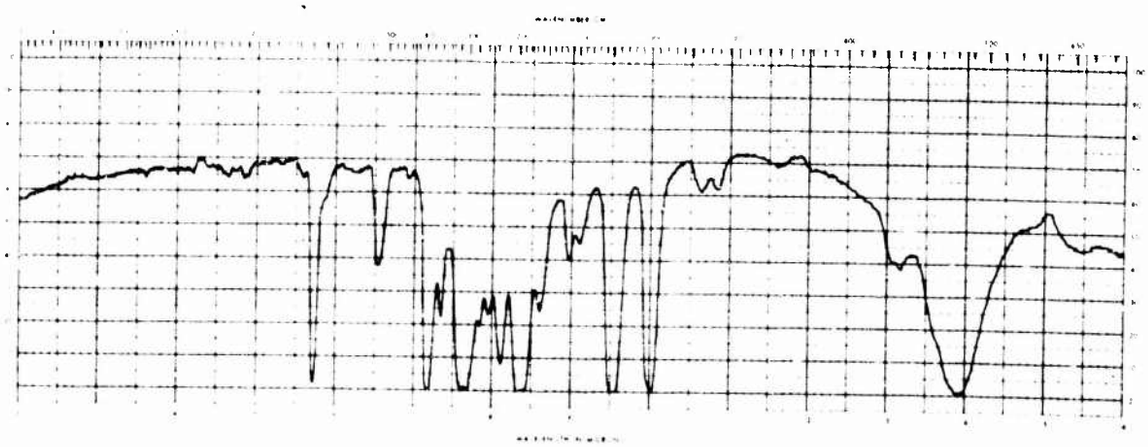


Fig. A3. Perfluorothioacetone
(gas, 12 mm)

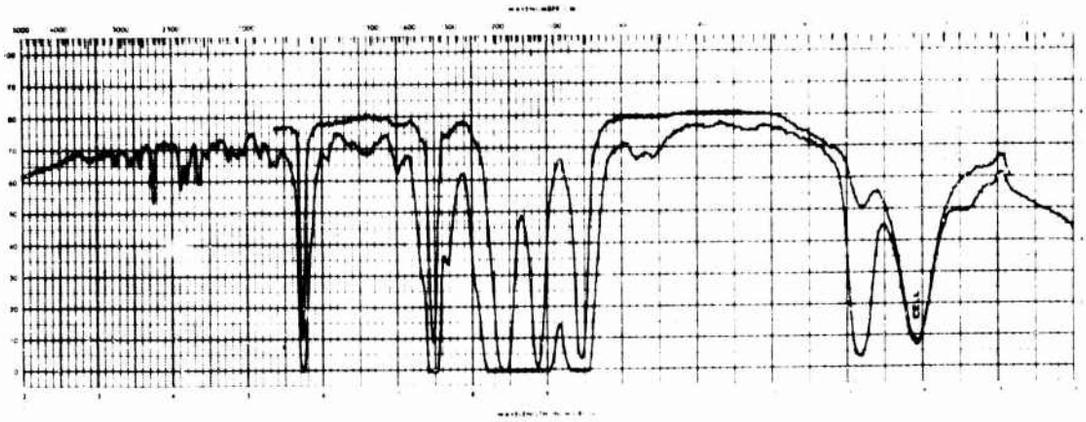


Fig. A4. Trifluoromethyl Trifluorovinyl Sulfide
(gas, 4 and 60 mm)

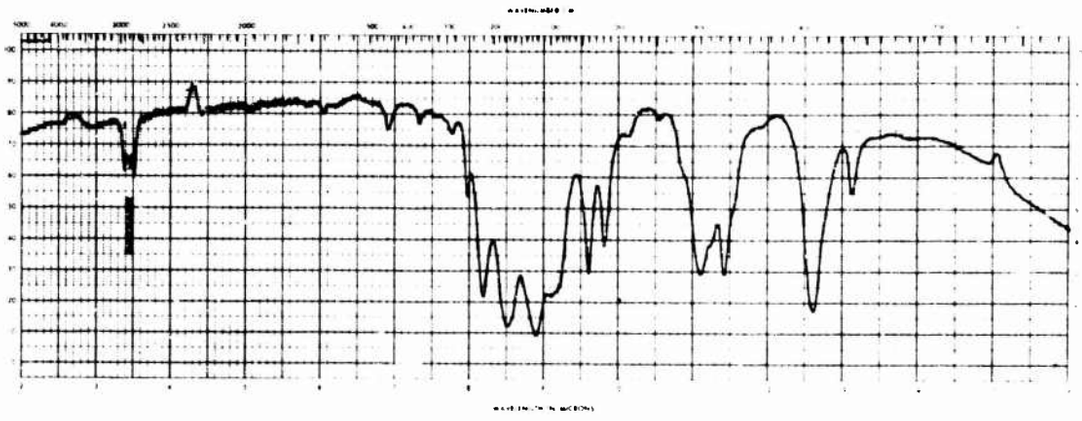


Fig. A5. Trifluoromethyl 2,2-Dichloro-1,1,2-
Trifluoroethyl Sulfide
(liquid)

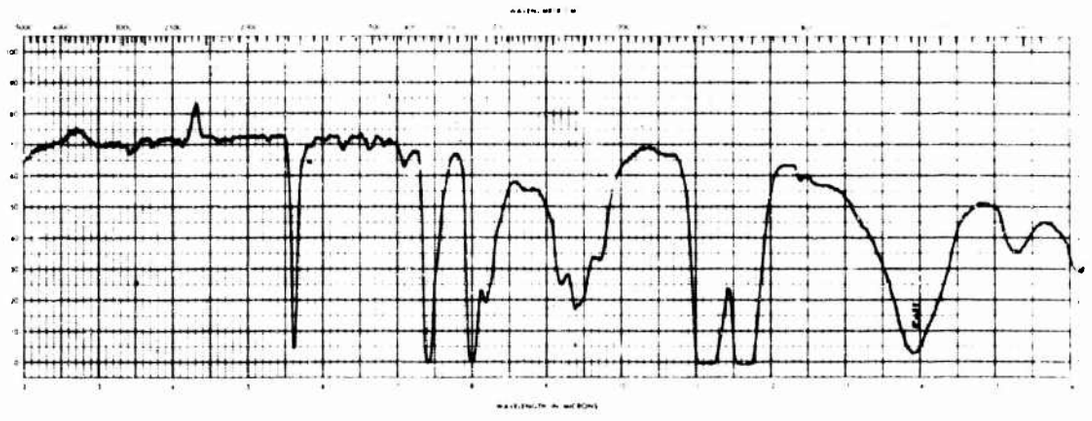


Fig. A6. Trifluorovinylsulfur Pentafluoride
(gas, 15 mm)

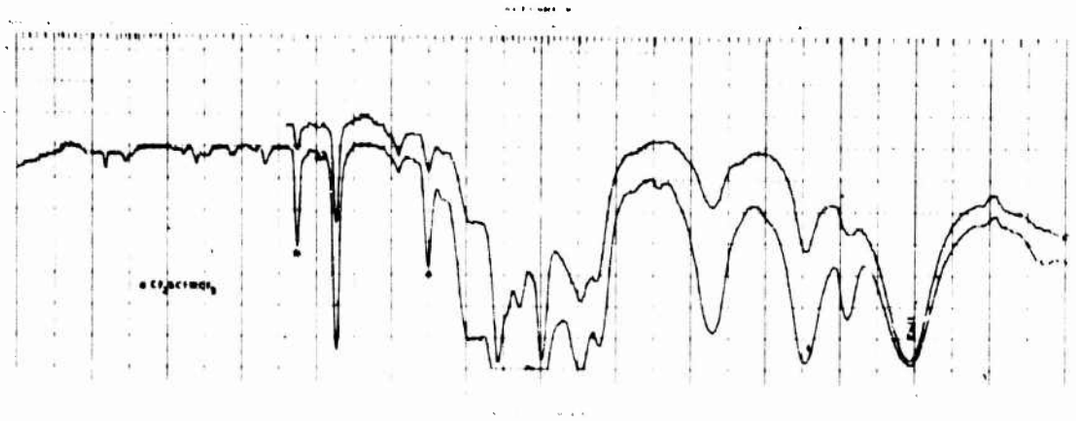


Fig. A7. 2-Chloro-1-nitroso-1,2,2-trifluoroethyl Trifluoromethyl Sulfide (gas, 2 and 12 mm)

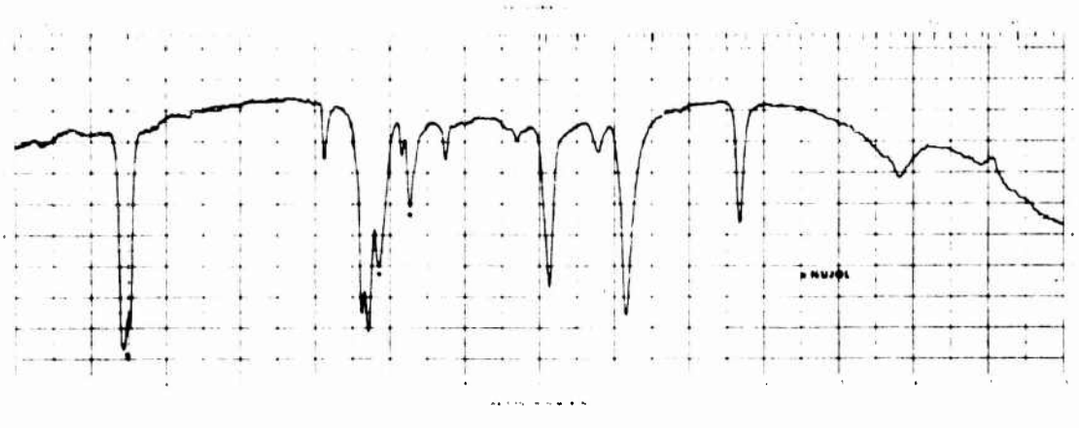


Fig. A8. Bis(pentafluorophenyl) Disulfide (Nujol mull)

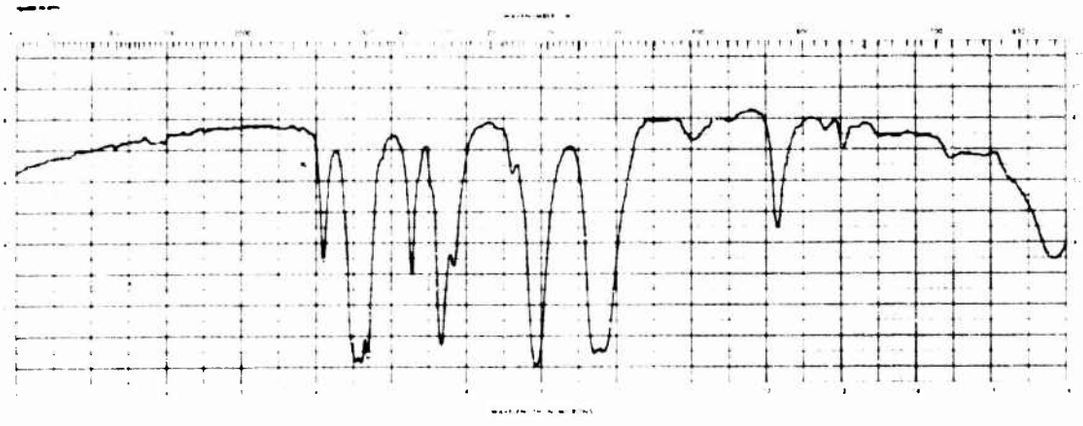


Fig. A9. Pentafluoronitrosobenzene (melt)

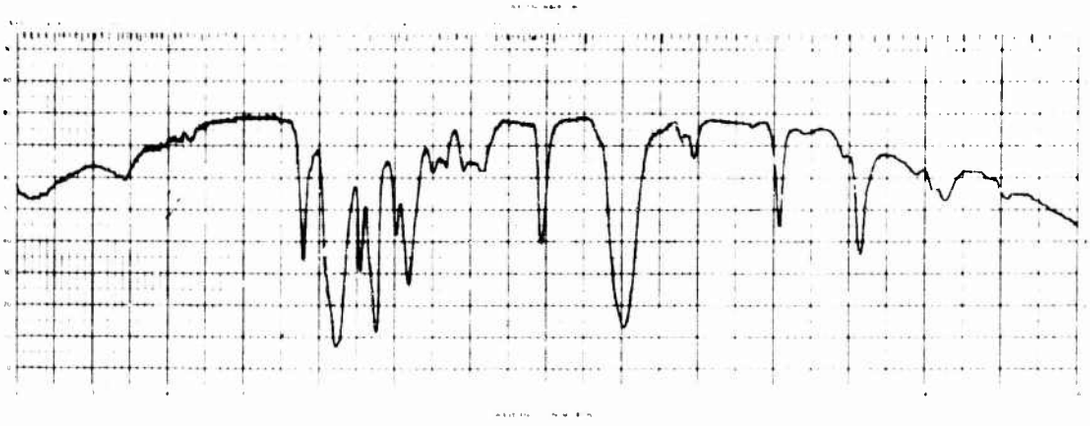


Fig. A10. Pentafluorobenzoyl Nitrite
(liquid)

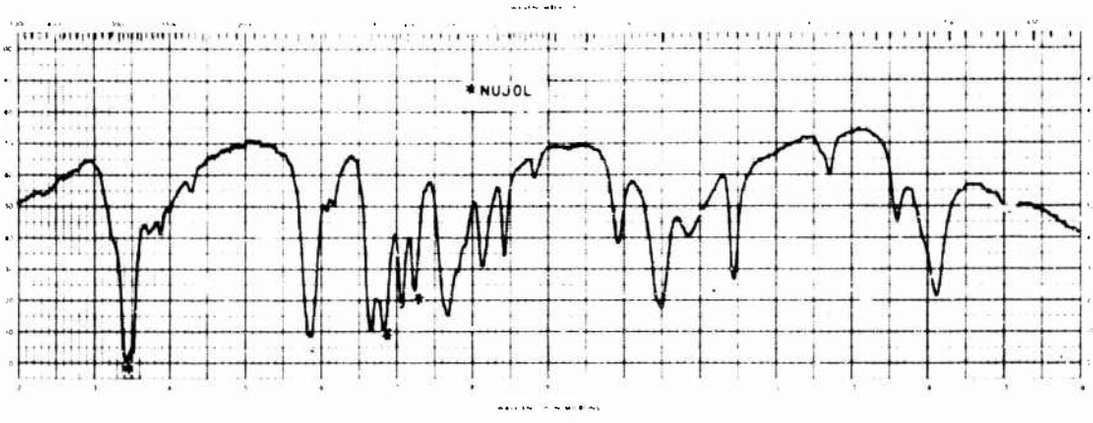


Fig. A11. Tetrafluoroterephthalyl Mononitrite
(Nujol mull)

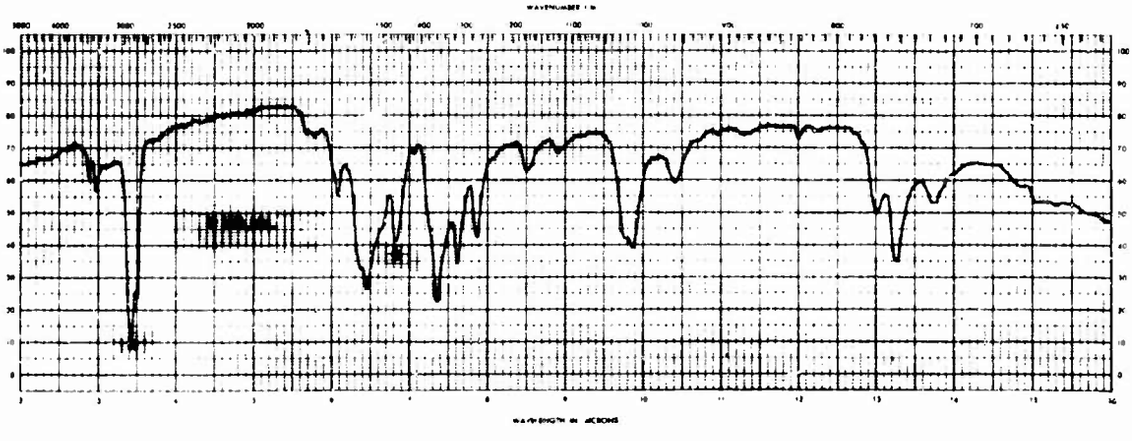


Fig. A12. p-Aminotetrafluoronitrosobenzene
(Nujol mull)

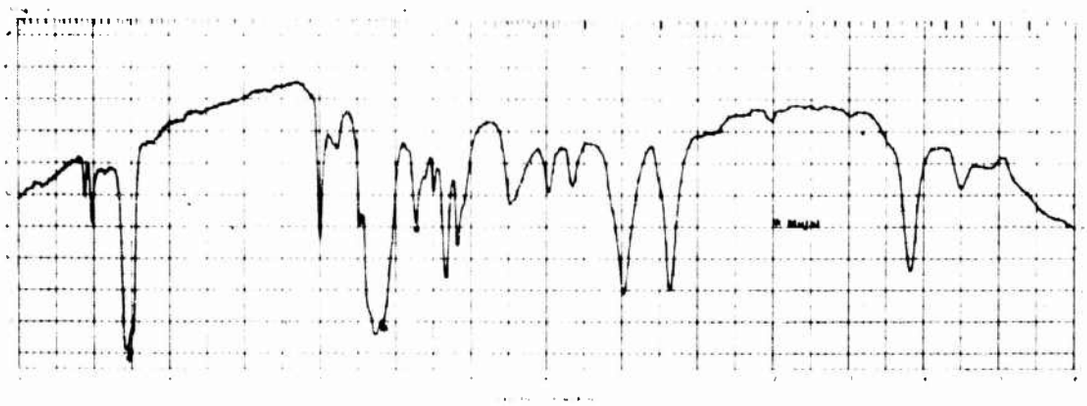


Fig. A13. 4,4'-Diaminooctafluorobiphenyl Oxidation Product (Nujol mull)

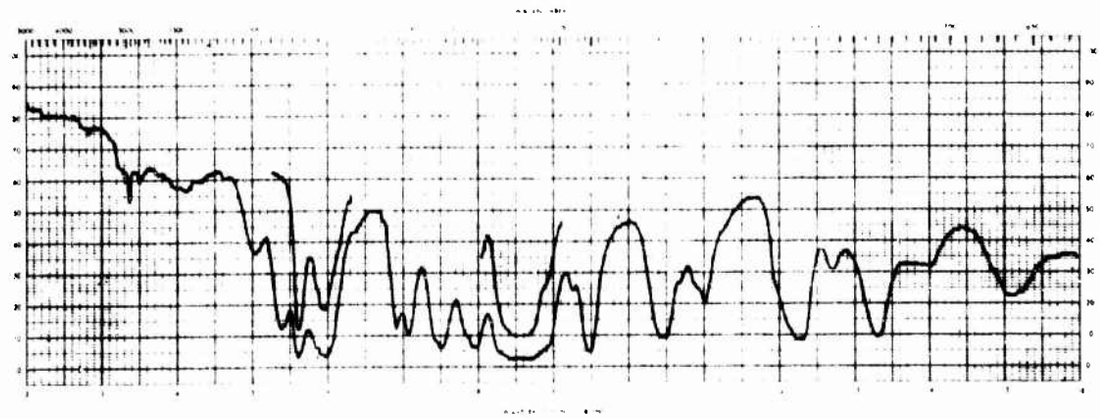


Fig. A14. 3-Carbomethoxyperfluoropropionyl Nitrite (liquid)

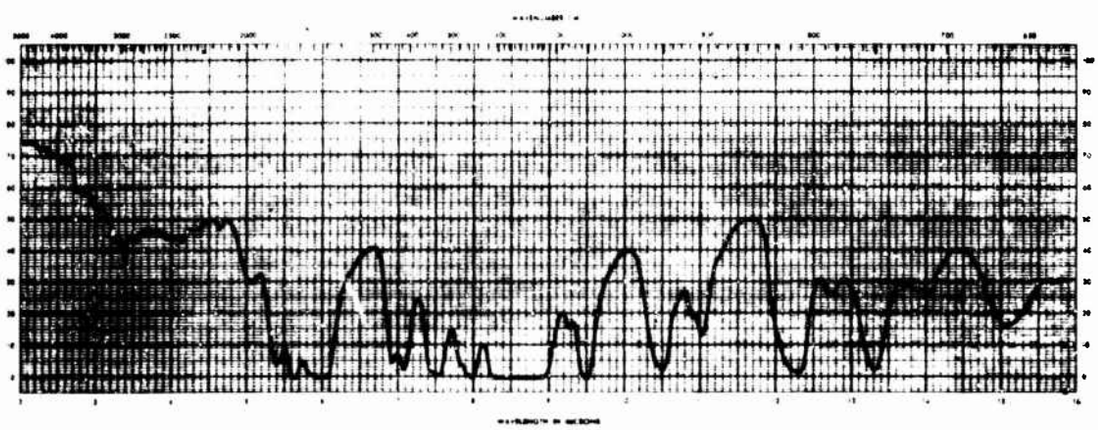


Fig. A15. 4-Carbomethoxyperfluorobutyryl Nitrite (liquid)

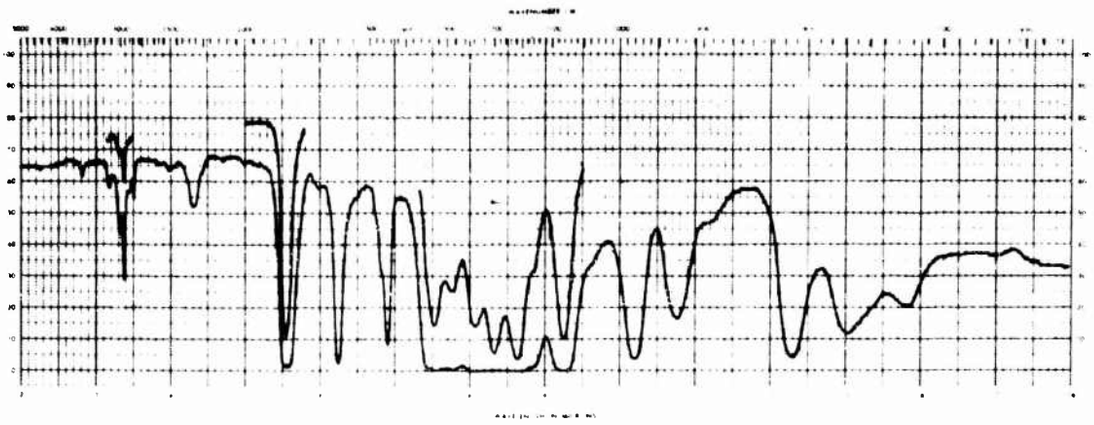


Fig. A16. Methyl 3-Nitrosoperfluoropropionate (gas, 10 and 75 mm)

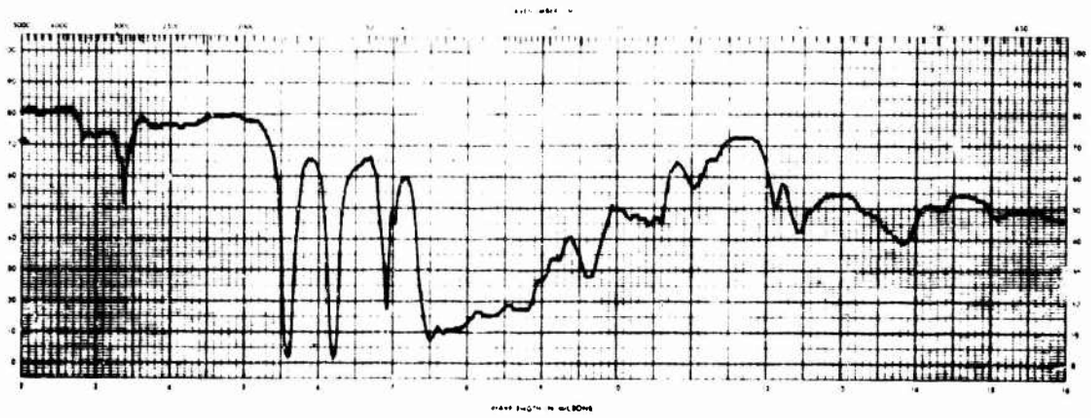


Fig. A17. Methyl 4-Nitrosoperfluorobutyrate (liquid)

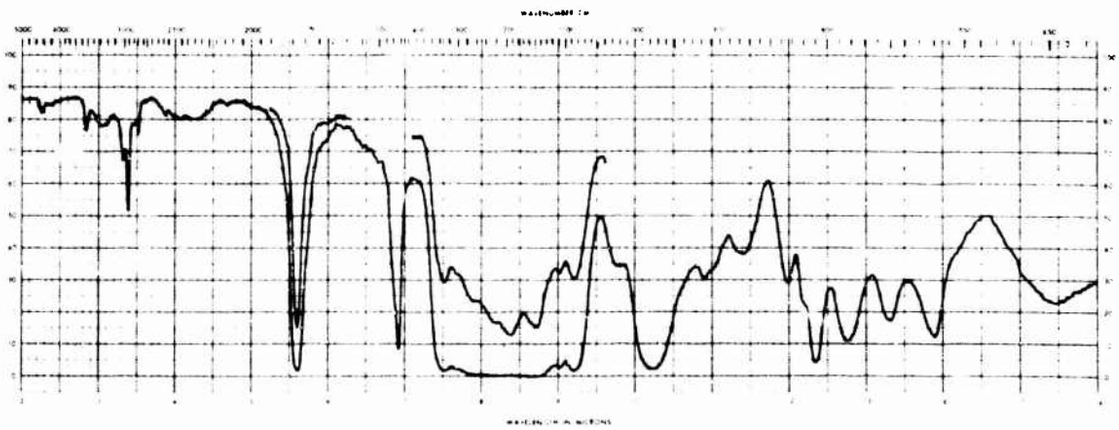


Fig. A18. $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$ (liquid)

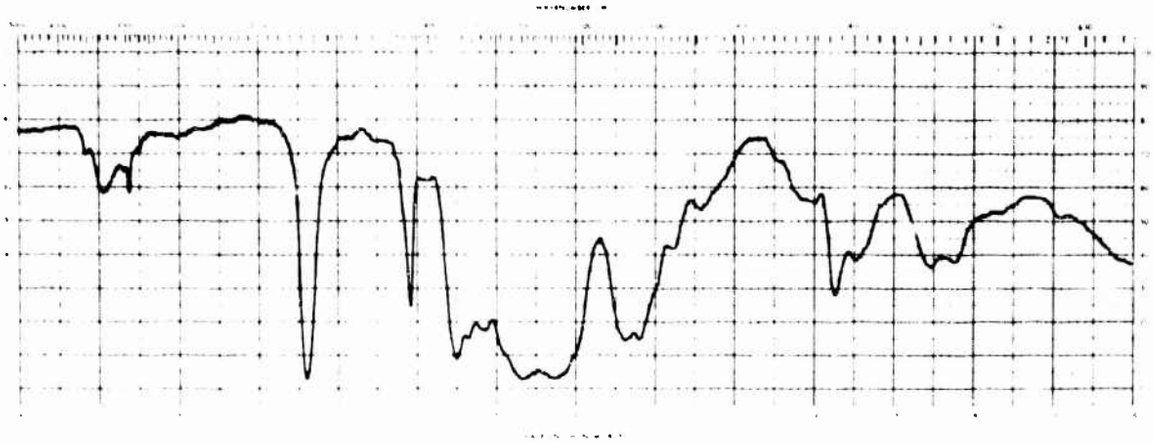


Fig. A19. $[CH_3O_2C(CF_2)_2]_2NO(CF_2)_2CO_2CH_3$
(liquid)

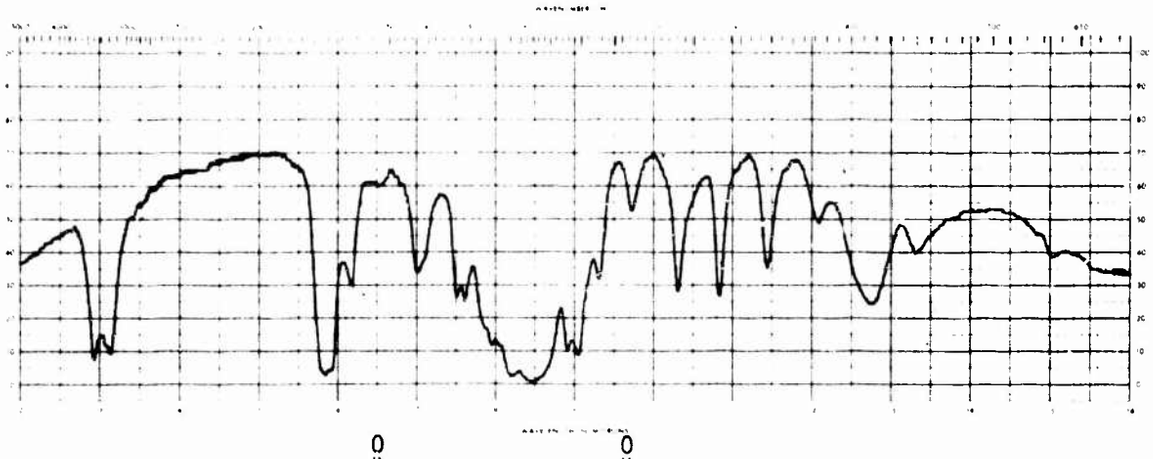


Fig. A20. $[H_2NC(=O)(CF_2)_3]_2NO(CF_2)_3C(=O)NH_2$
(KBr)

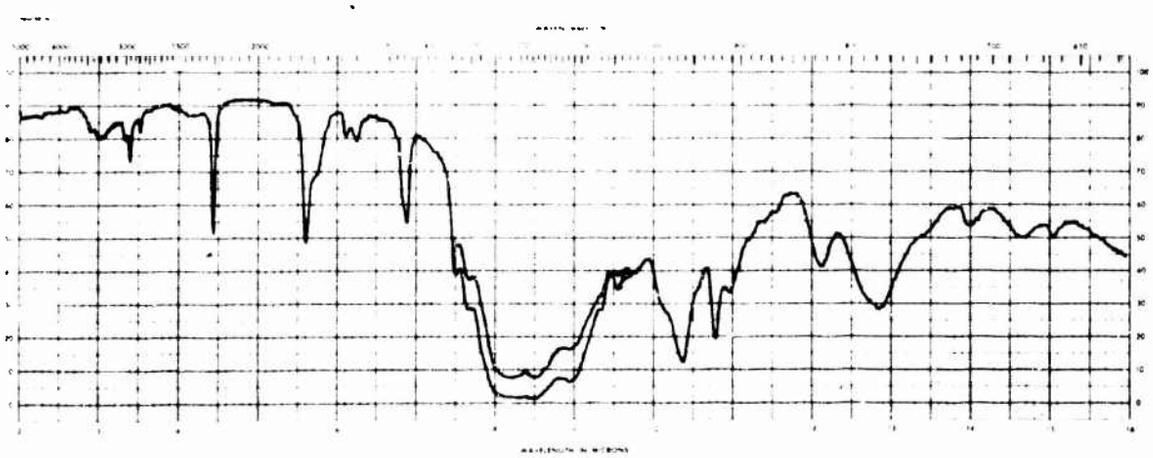


Fig. A21. $[NC(CF_2)_3]_2NO(CF_2)_3CN$
(liquid)

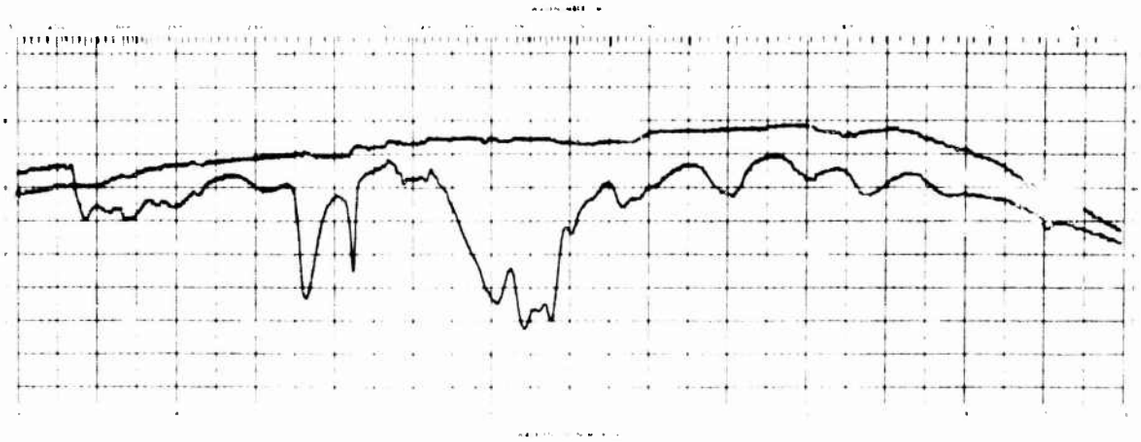


Fig. A22. 4-Nitrosoperfluorobutyric Acid (liquid)

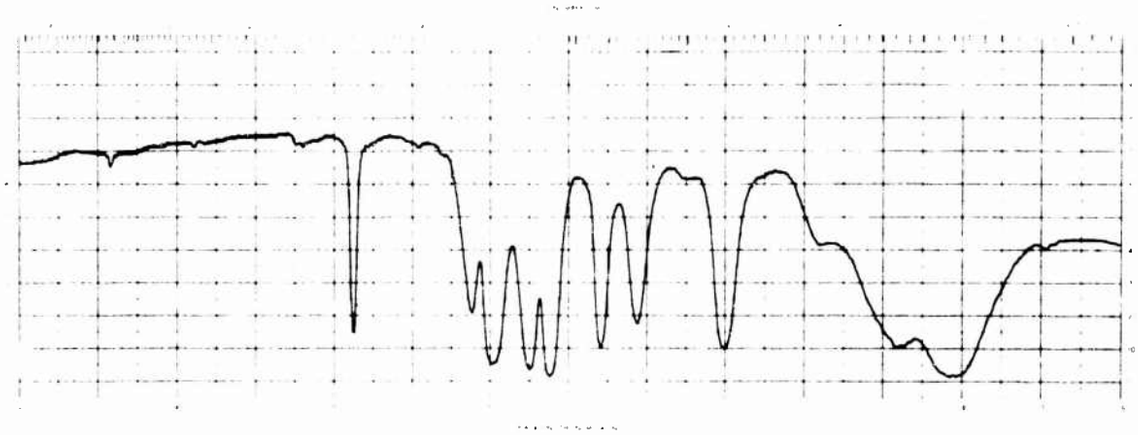


Fig. A23. 1-Bromo-1,1,2,2-tetrafluoro-2-nitrosoethane (gas, 15 mm)

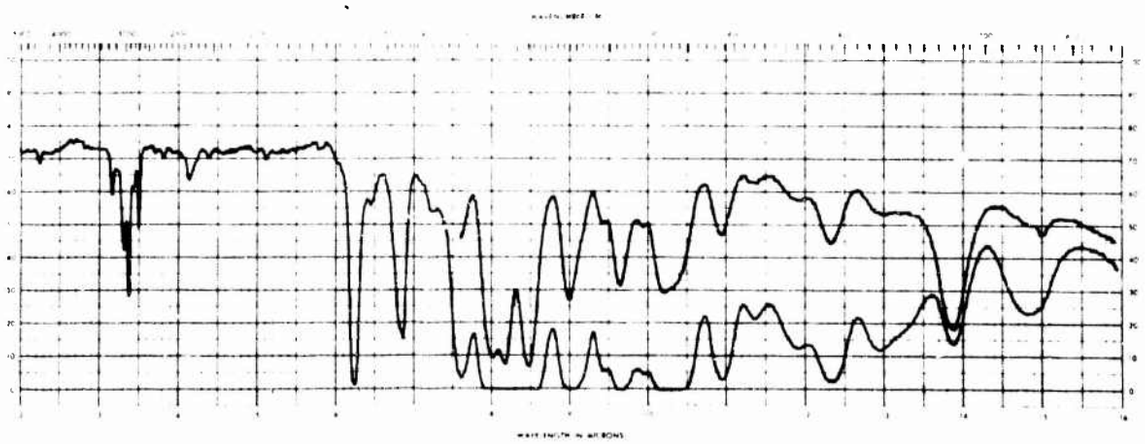


Fig. A24. Methyl 1-Chloro-1,2,2-trifluoro-2-nitrosoethyl Ether (gas, 3 and 24 mm)

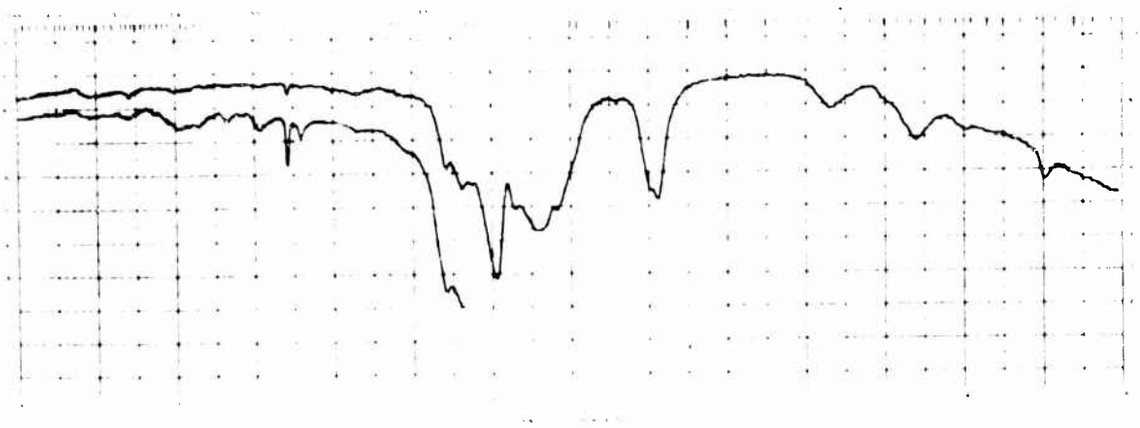


Fig. A25. $C_3F_7O[CF(CF_3)CF_2O]_3CF=CF_2$
(liquid)

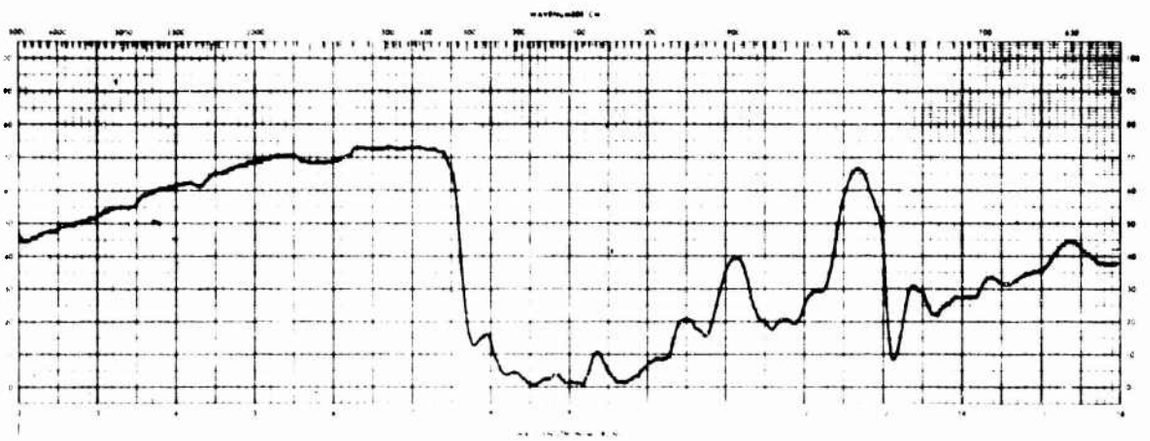


Fig. A26. $CF_3NO/CF_3SCF=CF_2$ Copolymer
(solid)

Fig. A27. $CF_3NO/CF_2=CFBr$ Copolymer
(solid)

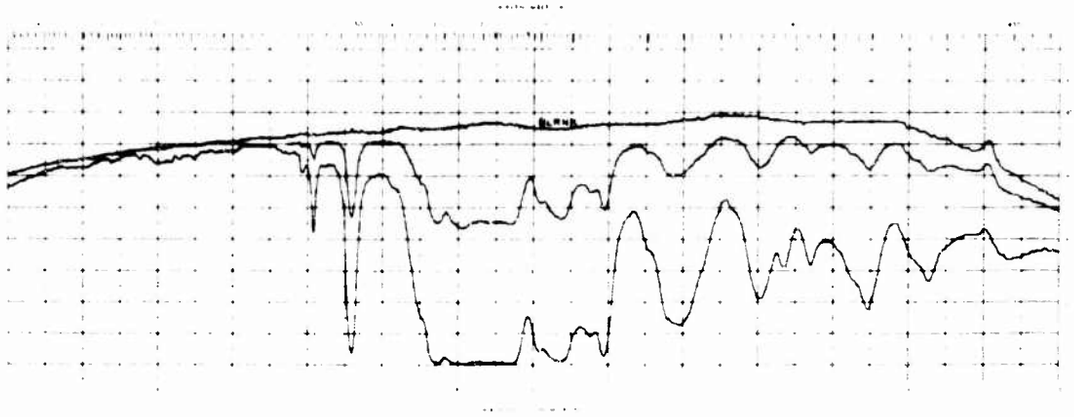


Fig. A28. $CF_3NO/CF_2{=}CF_2/C_6F_5NO$ Terpolymer (solid)

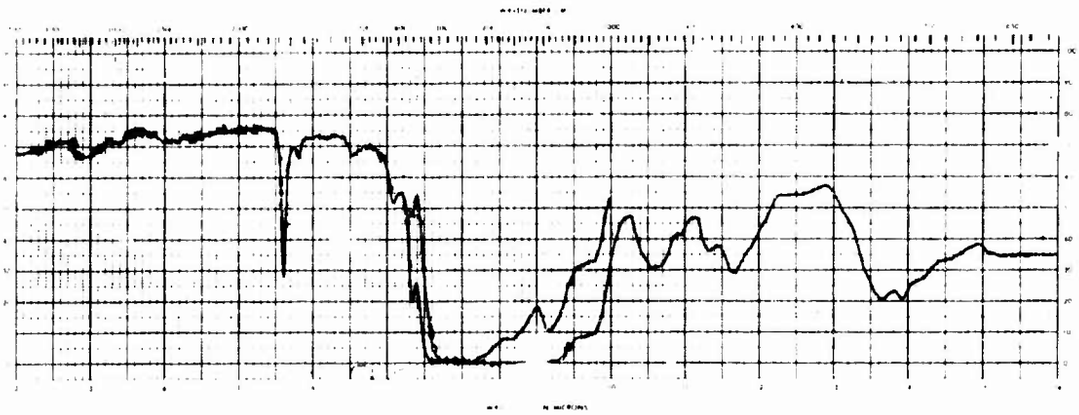


Fig. A29. $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCF{=}CF_2$ Terpolymer (solid)

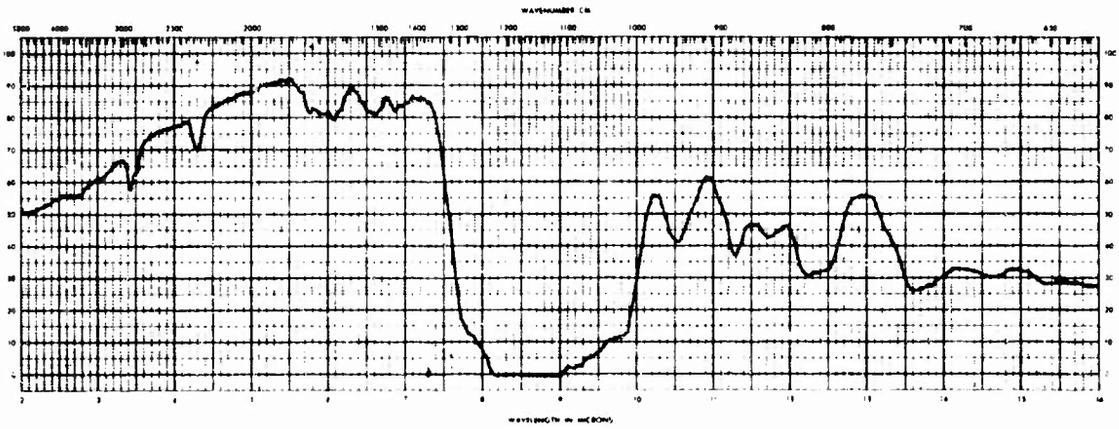


Fig. A30. $CF_3NO/CF_2{=}CFCF{=}CF_2$ Copolymer after Reaction with CF_3OF (solid)

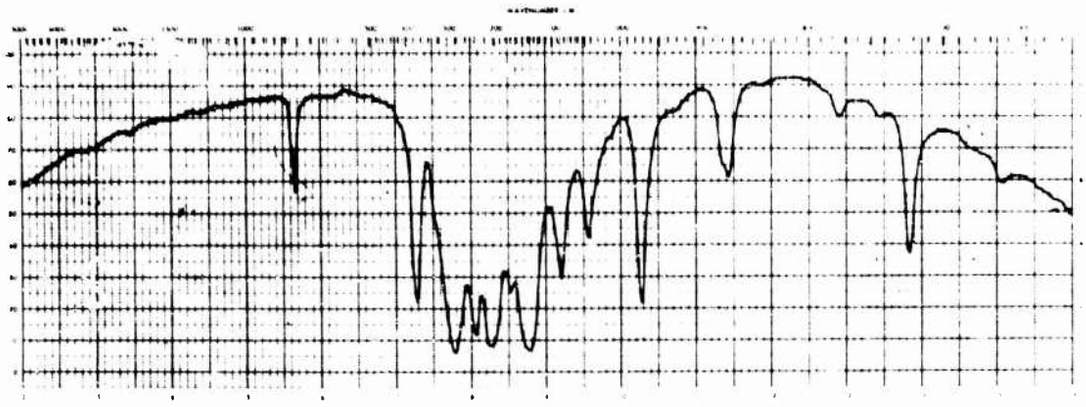


Fig. A31. $CF_3NCF_2CF{=}CFCF_2$ (O bridge) (liquid)

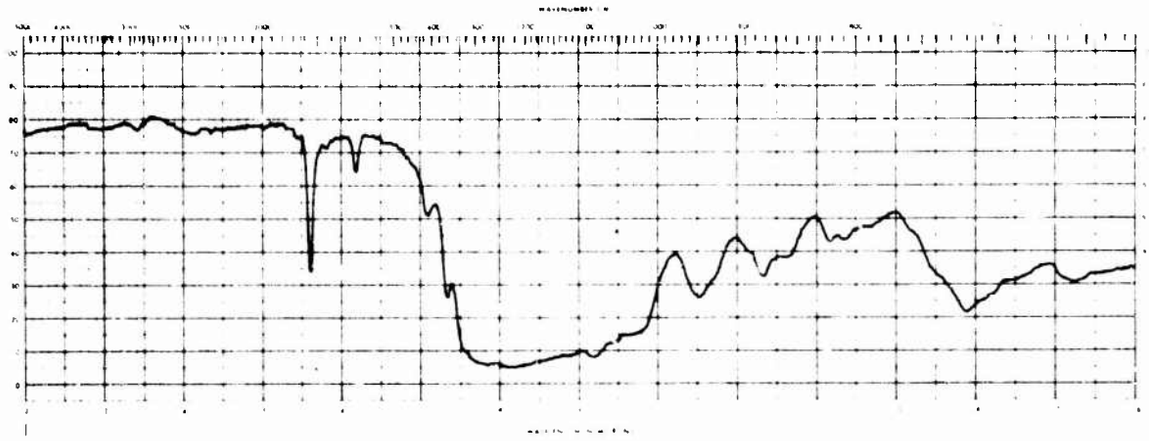


Fig. A32. $CF_3NO/CF_2{=}CFCF{=}CF_2$ Copolymer after Reaction with ClNO (solid)

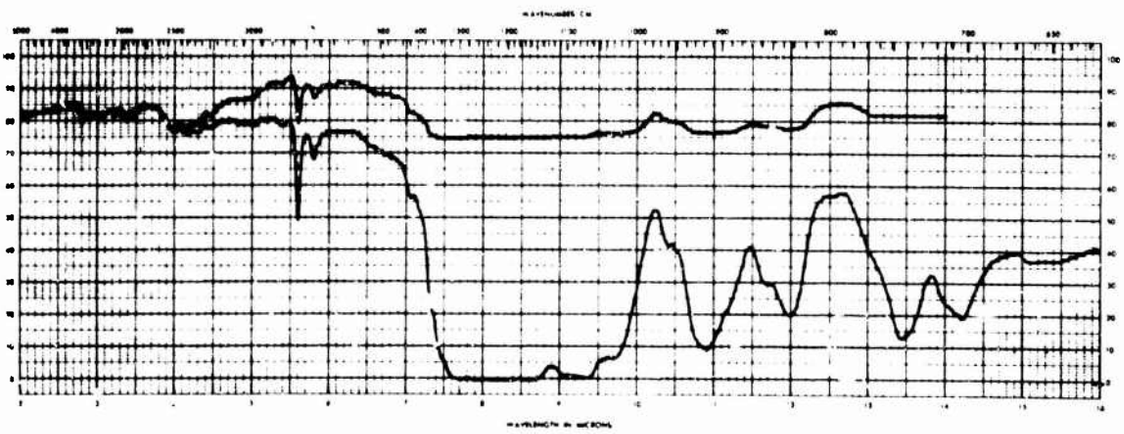


Fig. A33. $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCH{=}CH_2$ Terpolymer (solid)

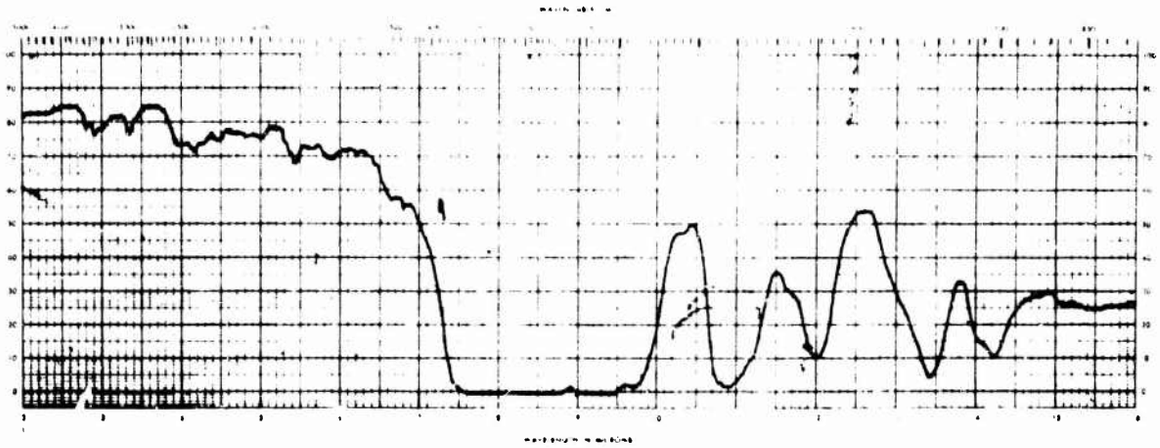


Fig. A34. $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCH{=}CH_2$ Terpolymer after Reaction with CF_3OF (solid)

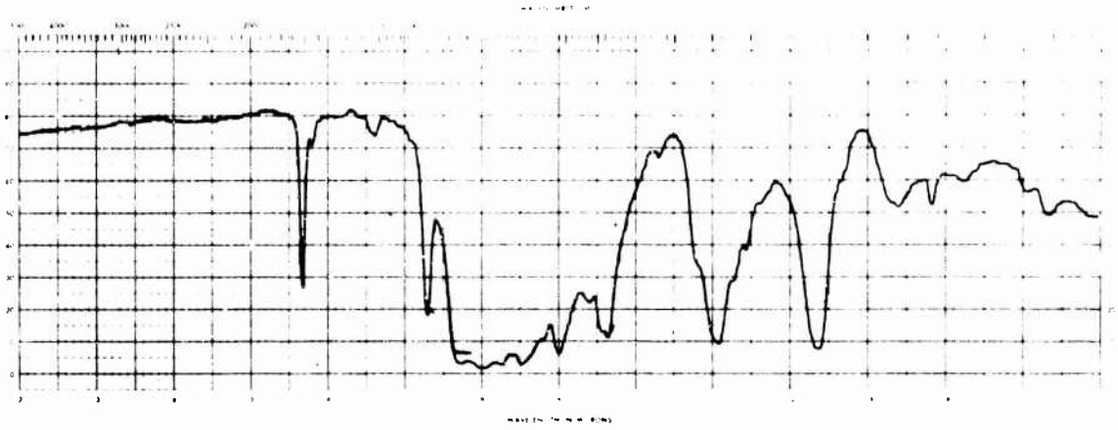


Fig. A35. $CF_3NO/CF_2{=}CF_2/CF_2{=}C{=}CF_2$ Terpolymer (solid)

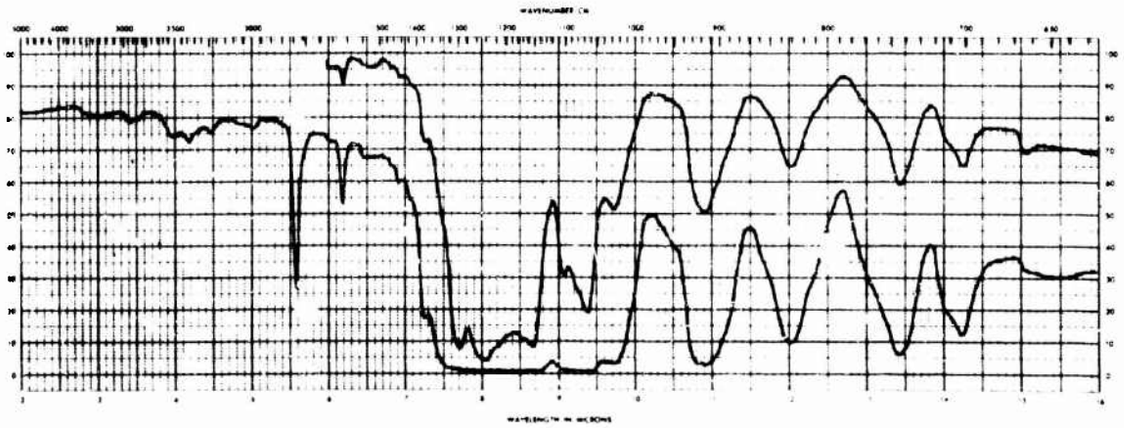


Fig. A36. $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCF_2NO$ Terpolymer (solid)

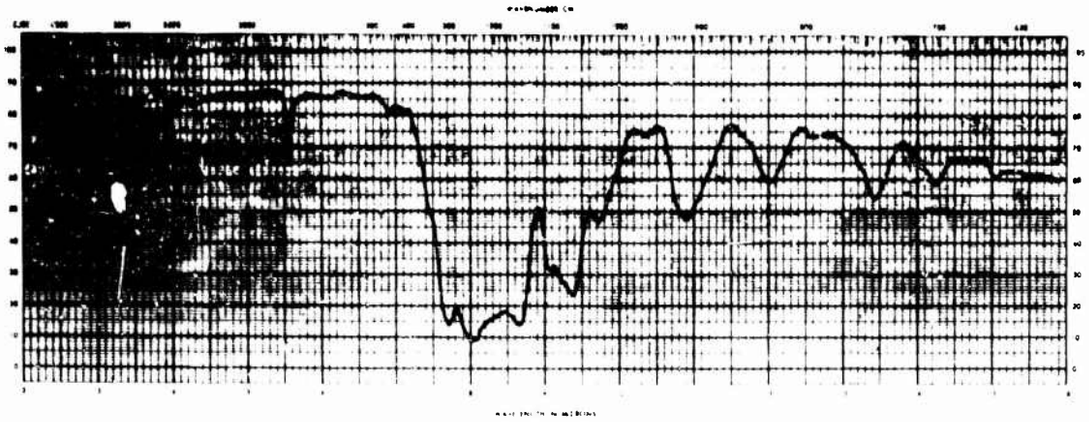


Fig. A37. $CF_3NO/CF_2{=}CF_2/CH_3O_2C(CF_2)_3NO$ Terpolymer
(5 mole % ester, solid)

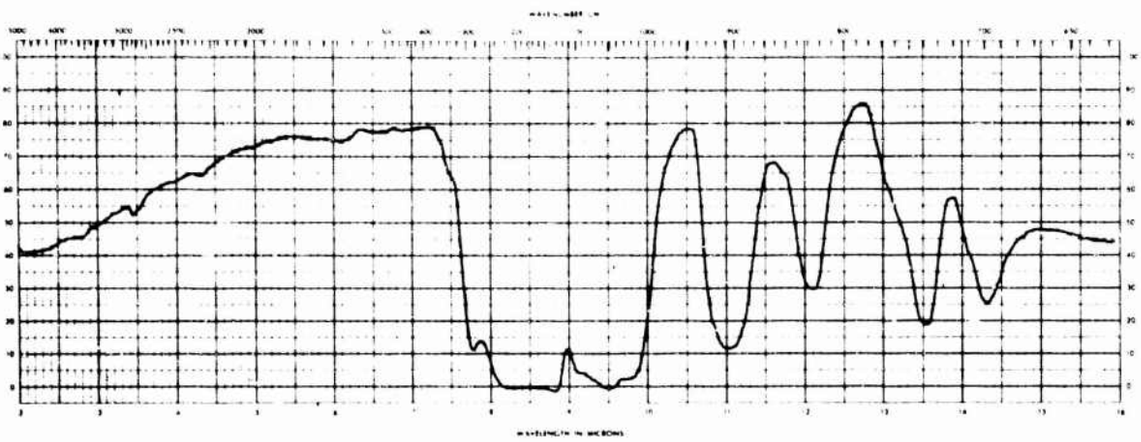


Fig. A38. $CF_3NO/CF_2{=}CF_2/CH_3OCF{=}CF_2$ Terpolymer
(10 mole % ether, solid)

APPENDIX B

NMR ANALYSIS OF MONOMERS

No.	Assignment	Peak	Peak Area	CHEMICAL SHIFT F(ppm) Reference CF_3COH	$CFCl_3$	$CF_2ClCFCl_2$	H(tau) Reference $(CH_3)_4Si$	CH_3CH	Pattern	J cps	Remarks
1.	$CF_3SCF=CF_2$	A	0.29	-32.7					4°	2.7	
	A D B (F trans to S)	D	0.10	+ 6.9					4°,2°,2°	2.7,29.0,40.8	
	C (F cis to S)	C	0.09	+25.5					4°,2°,2°	2.4,28.1,122.1	
		D	0.12	+76.7					4°,2°,2°	2.4,41.4,122.2	
2.	$CF_3SCF(NO)CF_2Cl$	A	3.0	-42.8					2°,3°	9.7,1.7	
	A C B	B	1.9	-14.0					NEQQ,2°,4°	13.3,1.76	
		C	0.9	+59.0					3°,4°	13.2,9.6	
3.	$CF_3\overline{NCF_2CF=CFCF_2O}$	A			+67.4				3°	11.5	
	A C D E B	B			+86.9				2°,2°	18.3,11.5	
		C			+99.6				5°,2°	11.2,16.5	
		D			+155.4				3°,3°	17.0,11.7	
		E			+157.3				3°,3°	17.7,9.0	
4.	$CH_3O\overset{O}{\overset{\|}{C}}\underbrace{CF_2CF_2}_{A,B}\overset{O}{\overset{\|}{C}}ONO$	A	3.7	+41.5					2°	4.2	
	C A,B	B	3.1	+47.2					1°		
		C						6.44	1°		
5.	$CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2\underbrace{CF_2}_{A}\overset{O}{\overset{\|}{C}}ONO$	A	15.9	+41.7					1°		
	C B A	B	8.0	+47.5					1°		
		C						6.45			

APPENDIX B (Cont'd)

NMR ANALYSIS OF MONOMERS

No.	Assignment	Peak	Peak Area	CHEMICAL SHIFT F(ppm) Reference CF_3COOH	$CFCl_3$	$CF_2ClCFCl_2$	CHEMICAL SHIFT H(τau) Reference $(CH_3)_4Si$	CH_3CO	Pattern	J cps	Remarks
6.	$CH_3OCCF_2CF_2NO$ (C; A,B)	A	5.7	+40.2					Barely resolvable doublet		
		B	5.8	+43.3							
		C						6.83	1°		
7.	$CH_3OCCF_2CF_2CF_2NO$ (D; C; A,B)	A	7.3	+38.9					A_2B_2 Pattern		
		B	7.2	+42.9							
		C	7.1	+48.9					1°		
		D						6.88	1°		
8.	$(CH_3OCCF_2CF_2CF_2)_2NOCF_2CF_2CF_2COCH_3$ (G D B,C A D G; E,F)	A	2.6	+10.2					Broad		
		B,C	4.7	+17.2					Broad		
		D	9.0	+41.2					Broad		
		E	5.1	+43.5					Broad		
		F	2.5	+47.8					Broad		
		G						6.22	1°		
9.	$(H_2NCCF_2CF_2CF_2)_2NOCF_2CF_2CF_2CNH_2$ (G D B,C A D G; E,F)	A	2	+8.7							
		B	4	+14.9							
		C		+17.3							
		D	6	+40.0							
		E	4	+42.1							
		F	2	+45.8							
		G						2.36			

APPENDIX B (Cont'd)

NMR ANALYSIS OF MONOMERS

No.	Assignment	Peak	Peak Area	CHEMICAL SHIFT F(ppm) Reference $CF_3\overset{O}{\overset{\|}{C}}OH$	$CFCl_3$	$CF_2ClCFCl_2$	CHEMICAL SHIFT H(tau) Reference $(CH_3)_4Si$	$CH_2\overset{O}{\overset{\|}{C}}H$	Pattern	J cps	Remarks
10.	$(NCCF_2CF_2CF_2)_2NOCF_2CF_2CF_2CN$ D B,C A D E,F	A	3.0	+9.70							G=impurity
		B	3.5	+14.5							H=residual peak
		C	3.5	+19.4							from $-\overset{O}{\overset{\|}{C}}NH_2$ of
		D	9.9	+28.2							parent compound
		E	6.0	+43.1							
		F	3.0	+47.3							
		G	small	+51.4							
		H					3.40				
11.	$CF_3SCF_2CFCl_2$ A C B	A	53	-41.3					3°,2°	9.9,2.6	
		B	18.5	-6.63					3°,4°	11.7,2.6	
		C	37	+0.29					4°,2°	9.9,11.7	
12.	$CF_3SCFClCF_2Cl$ A C B	A	46	-40.3					2°,3°	10.0, 5.3	
		B	32	-11.9					2°,4°	12.7, 5.2	
		C	16.5	+9.61					3°,4°	12.7, 10.0	
13.	$O_2NCF_2CF_2NO$ B A	A	2.6			+20.8			Broad		
		B	2.5			+38.3			Broad		
14.	Mixture CF_2BrCF_2NO $O_2NCF_2CF_2NO$ A C B D	A	2.2		+66.3				3°	4.15	
		B	2.3		+98.5				3°	11	
		C	2.0		+114.0				3°	4.1	
		D	2.0		+116.2				3°	1.8	

APPENDIX B (Cont'd)

NMR ANALYSIS OF MONOMERS

No.	Assignment	Peak	Peak Area	Chemical Shift F(ppm) Reference $CF_3\overset{O}{\overset{\|}{C}}OH$	$CFCl_3$	$CF_2ClCFCl_2$	Chemical Shift H(tau) Reference $(CH_3)_4Si$	$CH_3\overset{O}{\overset{\|}{C}}H$	Pattern	J cps	Remarks
15.	$CH_3OCFClCF_2NO$ C A B	A	1.0	-4.4					2°,2°	2.9, 6.2	
		B	1.8	+38.0					NEQQ		
		C						6.25	1°		
16.	$CF_3\overbrace{NCF_2CF_2O}$ A C B	A	3.00	-5.8	+70.1				3°,3°	7.7, 2.5	
		B	2.23	+6.7	+82.9				2°,4°	7, 2.7	
		C	1.77	+22.8	+98.8				Broad		
17.	$CF_2{=}CFCF{=}CF_2 + H_2O_2 \longrightarrow$	A	43	-1.66					2°,3°	14.1,2.9	
		B	40	+14.5					2°, + more	17.8	
	$\overbrace{CF_2CF_2CH{=}CF}$ or $\overbrace{CF_2OCF_2CH{=}CF}$ A,B D C A,B D C	C	20	+50.5							
		D						4.43	3°,3°,2°	18.1,13.7,7.9	
18.	$CF_2{=}CFCF{=}CFH$ A,B D E C F	A	1		+95.8				2°,2°	49, 30	
		B	1		+108.5				2°,2°	111, 49	
		C	1		+165				2°,2°	134, 69	
		D	1		+170.8				2°,2°	134, 29	
		E	1		+184.6				2°,3°,2°	111, 30, 10	
		F						3.15	2°,2°	72, 4	
19.	$CH_2{=}CHCH_2OCF_2CF_2H$ A B	A	1	+14.8					3°,2°	5.6, 2.8	
		B	1	+60.2					2°,3°	53, 56	

APPENDIX B (Cont'd)

NMR ANALYSIS OF MONOMERS

No.	Assignment	Peak	Peak Area	CHEMICAL SHIFT F(ppm) Reference $CF_3\overset{O}{\overset{\|}{C}}OH$	$CFCl_3$	$CF_2ClCFCl_2$	H(tau) Reference $(CH_3)_4Si$	$CH_3\overset{O}{\overset{\|}{C}}H$	Pattern	J cps	Remarks
20.	$CF_3CF_2CF_2O(\overset{\overset{A}{CF_3}}{\overset{\|}{C}}FCF_2O)_2CF{=}CF_2$ (B F A H A G D; A: B C; A: B C; D: E)	A	7.9	+3.9					Broad		
		B	4.5	+5.5					Broad		
		C	2.1	+8.2					Broad		
		D	1.1	+38.7					Part of F-vinyl		
		E	1.0	+46.2					Part of F-vinyl		
		F	2.0	+52.9					Part of F-vinyl		
		G	1.0	+59.7					Part of F-vinyl		
		H	2.1	+67.5					3°,+ unresolved		
		I	20				8.42		2°,2°	17, 4	Solvent
		J	2				4.3		2°	14	
		K	1				4.4		2°	12	
21.	$CF_3CF_2CF_2O(\overset{\overset{A}{CF_3}}{\overset{\|}{C}}FCF_2O)_3CF{=}CF_2$ (A F C H B G D,E)	A	13.3	+3.5					Broad		
		B	5.0	+5.3					3°		
		C	2.0	+7.9					Broad		
		D	1.0	+39.1					2°,2°	85, 66	
		E	1.0	+46.4					2°,2°	85, 111	
		F	2.0	+53.1					1°		
		G	1.0	+60.2					2°,2°	111, 66	
		H	33	+67.7					Irreg.Quartet		
		I	1				8.27		2°		Solvent
		J	1				8.55		2°		
22.	$(CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2)_2NOCF_2CF_2\overset{O}{\overset{\|}{C}}OCH_3$ (E C B A C E; B: D; C: D)	A	8.0	+12.7					Broad		Impure sample made area measurement in peaks C & D inaccurate.
		B	16.0	+19.8					2°	56	
		C	19.9	+39.5					Broad		
		D	19.3	+43.1					Broad		
		E						6.24	1°		

APPENDIX C

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm)Ref. $CF_3\overset{O}{\overset{\|}{C}}OH$	CHEMICAL SHIFT H(tau)Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(tau)Ref. $CH_3\overset{O}{\overset{\|}{C}}H$	Pattern & Splitting	Area	Assignment	Remarks
1.	$CF_3NO/CF_2{=}CF_2/CH_3OCFClCF_2NO$	A	-12.8			Broad	4.0	CF_3-N	
		B	+ 3.7			Broad	0.1	Probably CFCl	
		C	+10.6			Singlet	2.9	CF_2	
		D	+13 4			Broad	0.3	CF_2	
	4 : 5 : 1	E	+20.4			Superposition of two broad peaks	1.5	CF_2 + CF_2NO	
		F	+23.2			Broad	2.3	CF_2	
		G		6.26		Singlet	3	OCH_3	
		H		8.37		Singlet	1		
		I		9.00		Singlet	1		
2.	$CF_3NO/CF_2{=}CF_2/CH_3OCF{=}CF_2$	A	-12.7			Broad	12.4	CF_3-N	
		B	+ 4.3			Singlet	Very small		
		C	+ 6.5			Broad	0.5	CF_2 attached to 2 oxygens	
		D	+10.8			Broad	6.6	CF_2	
	5 : 4 : 1	E	+13.5			Broad	1.0	CF_2	
		F	+20.9			Broad	1.2	CF_2	
		G	+23.1			Broad	6.9	CF_2	
		H		6.58		Singlet	1	OCH_3	
		I		8.28		Singlet	0.2		
		J		9.01		Singlet	0.2		
3.	$CF_3NO/CF_2{=}CF_2$	A	-12.4			Broad	4.5	CF_3-N	
		B	+10.8			Broad	3.0	CF_2	
		C	+13.3			Broad	0.5	CF_2	
	1 : 1	D	+20.9			Broad	0.4	CF_2	
		E	+23.1			Broad	2.8	CF_2	
4.	$CF_3NO/CF_2{=}CFBr$	A	-15.8				8	CF_3-N	Because peak B is very broad, the quantitative values are very uncertain
		B	-13.4				40	CF_3-N	
	1 : 1	C	+14.8			Very broad	30	CF_2,CFBr	

APPENDIX C (Cont'd)

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm)Ref. $CF_3\overset{O}{\overset{\|}{C}}OH$	CHEMICAL SHIFT H(tau)Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(tau)Ref. $CH_3\overset{O}{\overset{\|}{C}}H$	Pattern & Splitting	Area	Assignment	Remarks
5.	$CF_3NO/CF_2=CF_2/CF_2=CFBr$	A	-12.4				69	CF_3-N	
		B	+11.1				30	CF_2	
		C	+13.9				5	CF_2	
	6 : 5 : 1	D	+16.0				5	CFBr	
		E	+21.3				4	CF_2	
		F	+23.6				29	CF_2	
6.	$CF_3NO/CF_2=CF_2/CF_2=CFBr$	A	Shoulder on B					CF_3-N	
		B	-12.4				73	CF_3-N	
		C	+11.1				28	CF_2	
	6 : 4 : 2	D	+13.9				5	CF_2	
		E	+16.0				8	CFBr	
		F	+21.3				6	CF_2	
		G	+23.6				28	CF_2	
7.	$CF_3NO/CF_2=CF_2/CF_2=CFBr$	A	Shifts same as above				27	CF_3-N	
		B					9	CF_2	
		C,D					9	Mostly CFBr	
	6 : 3 : 3	E,F					10	CF_2	
8.	$CF_3NO/CF_3SCF=CF_2$	A	-42.9			Broad	1.2	CF_3S	Apparently backbone fluorine resonances are too broad to be seen
		B	-42.0			Broad			
	1 : 1	C	-13.2			Broad	1.0	CF_3-N	
9.	$CF_3NO/CF_2=CF_2/CF_3SCF=CF_2$	A	-40.9				10	CF_3S	
		B	-12.3				68	CF_3-N	
		C	+10.4				34	CF_2	
	6 : 5 : 1	D	+12.7				10	CF_2	
		E	+20.5				9	CF_2	
		F	+22.6				27	CF_2	

APPENDIX C (Cont'd)

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm)Ref. $CF_3\overset{O}{\overset{\|}{C}}OH$	CHEMICAL SHIFT H(tau)Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(tau)Ref. $CH_3\overset{O}{\overset{\|}{C}}H$	Pattern & Splitting	Area	Assignment	Remarks
10.	$CF_3NO/CF_2=CF_2/CF_3SCF(NO)CF_2Cl$	A	-42.5				0.09	CF_3S	
		B	-12.5				0.70	CF_3NO	
		C	+10.8				0.41	CF_2	
	2.63: 3.29 : 0.66	D	+13.5				0.06	CF_2	
		E	+21.1				0.07	CF_2	
		F	+23.2				0.37	CF_2	
11.	$CF_3NO/CF_2=CFCF=CF_2$	A	-11.7			Broad	60	CF_3	Very broad peaks
		B	+ 1.5			Broad	20	CF_2 in chain	make area values
		C	+16.1			Very broad base	33	CF_2 in chain	only estimates
	1 : 1	D	+48.9			Broad	4	$=CF_2$ pendent	
		E	+74.4			Broad	4	$=CF_2$ in chain	
		F	+76.4			Broad	8	$=CF_2$ in chain	
		G	+78.4			Broad	1	$=CF$ pendant	
12.	$CF_3NO/CF_2=CF_2/CF_2=CFCH=CH_2$	A	-12.1				165	CF_3-N	
		B	-10.4				20	CF_2-N	
		C	- 3.5				10	$=CF_2$	
		D	+11.1				77		
		E	+13.9				10		
		F	+18.8				19	CF_2	
		G	+21.2				14		
		H	+22.6				80		
		I	+28.3				6	CF_2	
		J	+42 to +47			Very broad	18	CF (all types)	
		K			3.8-4.9		177	$=CH$	
		L			5.2-5.8		130	CH_2 next to NO	
		M			6.0-6.5		3	CH_2 next to CF_2	

APPENDIX C (Cont'd)

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm)Ref. $CF_3\overset{O}{\overset{\|}{C}}OH$	CHEMICAL SHIFT H(tau)Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(tau)Ref. $CH_3\overset{O}{\overset{\|}{C}}H$	Pattern & Splitting	Area	Assignment	Remarks
13.	$CF_3NO/CF_2=CFCF=CF_2$) + CF_3OF	A	-12.2			Broad	289	CF_3-N	Unassigned peaks are $O-CF_2-O$ and backbone CF_2's, shifted in position by loss of unsaturation
		B	+ 1.4			Broad	43	CF_2 in chain next to double bond	
	1 : 1	C	+ 6.0			Broad	8		
		D	+10.5			Broad	25		
		E	+15.9			Broad	39	CF_2 in chain	
		F	+19.9			Broad	24		
		G	+23.0			Broad	17		
		H	+42.5			Broad	22		
		I	+46.4			Broad	22		
		J	+73.1			Broad	15	=CF	
		K	+75.6			Broad	14	=CF	
		L	+77			Broad	5	=CF	
14.	$CF_3NO/CF_2=CF_2/CF_2=C=CF_2$	A	-13.08			Shoulder on B	~2 to 3	CF_3-N	
		B	-12.32			Broad	~3 to 4	CF_3-N	
		C	- 2.35			Broad	0.5		
	2 : 1 : 1	D	+ 5.33			Broad	0.3		
		E	+10.28			Broad/Singlet	2.0	CF_2 in chain	
		F	+15.01			Broad/Singlet	0.3	CF_2 in chain	
		G	+20.21			Broad/Singlet	0.4	CF_2 in chain	
		H	+22.38			Broad/Singlet	2.0	CF_2 in chain	
15.	$CF_2=CF_2/C_6F_5NO$	A	+11.5			Broad	1	CF_2	Areas are only estimates
		B	+21.6			Broad	4	CF_2	
		C	+61.7			Broad	5	C_6F_5	
	1 : 1	D	+69.8			Broad	4	C_6F_5	
		E	+83.5			Broad	7	C_6F_5	

APPENDIX C (Cont'd)

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm) Ref. CF_3COOH	CHEMICAL SHIFT H(tau) Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(tau) Ref. CH_3COOH	Pattern & Splitting	Area	Assignment	Remarks
16.	$CF_3NO/CF_2=CF_2/C_6F_5NO$	A	-12.0			Broad	0.25	CF_3-N	
		B	- 9.4			2° x 9.1 cps.	0.33	CF_2	
		C	- 5.5			3° x 9.1 cps.	0.17	CF	
	9 : 11 : 3	D	+11.1			Broad	0.13	CF_2	
		E	+12.8			Broad	0.033	CF_2	
		F	+14.0			Broad	0.010	CF_2	
		G	+21.15			Broad	0.014	CF_2	
		H	+23.5			Broad	0.172	CF_2	
		I	+62.0			Broad	0.039	C_6F_5	
		J	+78.2			Broad	0.010	C_6F_5	
		K	+84.2			Broad	0.046	C_6F_5	
17.	$CF_3NO/CF_2=CF_2/CH_3O_2C(CF_2)_3NO$	A	-12.4			Broad	16.0	CF_3N	
		B	+10.9			Broad	8.7	CF_2O	
		C	+13.6			Broad	0.9	CF_2O	
	4 : 5 : 1	D	+21.0			Broad	1.6	CF_2N	
		E	+23.6			Broad	7.0	CF_2N	
		F	+41.7			Broad	2.0	$CF_2CF_2CF_2$	
		G	+43.5			Broad	2.0	$CF_2CF_2CF_2$	
		H		6.24		Singlet	2.7	OCH_3	
18.	$CF_2=CF_2/CF_2ClCFClNO$	A	-1. 0			Broad	2.5	CF_2Cl	Areas are approximations
		B	: 8.6			Broad	2	CF_2	
		C	+20.1			Broad (twin peaks)	2	CF_2	
	1 : 1	D	+25.9			Broad	1	CFCl-N	
19.	$(CF_3NO/C_2F_4/CF_2=CFCF=CF_2)+CF_3OF$	A	-24.3			Broad	42	CF_3O on backbone	
		B	-22.0			Broad	10	CF_3O on side chain	
		C	-12.7			Broad	77	CF_3N	
		D	+7.6,+9.7			Broad	31	OCF_2	
		E	+18.2			Broad	38	NCF_2	
		F	+41.7,+43.5			Broad	27	CF_2 not next to O + OCF	
		G	+62.2			Broad	8	CF in chain	

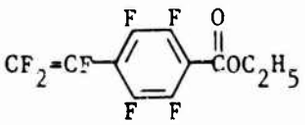
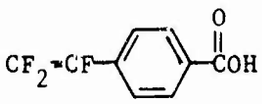
APPENDIX C (Cont'd)

NMR ANALYSIS OF POLYMERS

No.	Polymer & Mole Ratio of Monomer Charged	Peak	CHEMICAL SHIFT F(ppm)Ref. CF_3COH	CHEMICAL SHIFT H(t-u)Ref. $(CH_3)_4Si$	CHEMICAL SHIFT H(t-u)Ref. CH_3CH	Pattern & Splitting	Area	Assignment	Remarks
20.	$(CF_3NO/CF_2=CF_2/CF_2=CFCH=CH_2)+ CF_3OF$								
		A	-17.6			Broad	17	CF_3OCH, backbone	
		B	-15.0			Broad	6	CF_3OCH, side chain	
		C	-12.4			Broad	438	CF_3N	
		D	+10.9			Broad	220	CF_2	
		E	+13.3			Broad	26	CF_2	
		F	+21.0			Broad	30	CF_2	
		G	+23.5			Broad	221	CF_2	
		H	+50.9			Broad	4	CFH	
		I			5.5	One very weak absorption			

APPENDIX D

MONOMERS FROM OUTSIDE SOURCES

No.	Compound	Amount (g.)	Source
1.	$CF_2=CFCF_2OCH_2CF_3$	0.5	University of Florida
2.	$CF_2=CFCF_2\overset{\overset{O}{\|}}{C}OC_2H_5$	8	University of Florida
3.		5	University of Florida
4.		25	University of Florida
5.	$CF_2ClCF(NO)CH_2CH=CH_2$	1	University of Florida
6.	$CF_2=CFCF_2NO$	0.5	University of Florida
7.	$CF_2=C=CH_2$	41	University of Florida
8.	$CF_2=CFC_4H_9$	5	University of Florida
9.	$CF_2=CFCH_2CH=CH_2$	25	University of Florida
10.	$CF_2=CFSi(CH_3)_2OC_2H_5$	10	University of Florida
11.	$CF_2=CFCH_2CF_2CF_2CH_2CF=CF_2$	11	University of Colorado
12.	$CF_2=CHCF_2CH_2CF_2CH=CF_2$	6	University of Colorado
13.	$CF_2=CFCF_2\overset{\overset{O}{\|}}{C}OCH_3$	30	University of Colorado
14.	$CF_2=CFCF_2CFClCF_2CF=CF_2$	29	University of Colorado
15.	$CF_2=CFCF_2\overset{\overset{O}{\|}}{C}OK$	1	University of Colorado

APPENDIX E

POLYMER SAMPLES SUBMITTED

No.	Designation	Polymer	Charged Monomer Ratio	Amount (g.)
1.	Q.O.-A	$CF_3NO/CF_2=CF_2$	1:1	5
2.	Q.O.-B	" / "	1:1	5
3.	W.O.-63	" / "	1:1	54
4.	W.O.-67	" / "	1:1	60
5.	Q.C.-60.4	" / "	1:1	92
6.	Q.C.-60.5	" / "	1:1	80
7.	Q.C.-4.3	$CF_3NO/CF_2=CFBr$	1:1	5
8.	Q.C.-C	" / "	1:1	7.4
9.	Q.C.-8.1	$CF_3NO/CF_2=CF_2/CF_2=CFBr$	6:5:1	5
10.	Q.C.-8.2	" / " / "	3:2:1	5
11.	Q.C.-8.3	" / " / "	2:1:1	5
12.	Q.C.-8.9	" / " / "	6:5:1	20.4
13.	Q.C.-8.10	" / " / "	3:2:1	18
14.	Q.C.-8.11	" / " / "	2:1:1	27.3
15.	Q.C.-8.12	" / " / "	2:1:1	41.6
16.	Q.C.-12.2	$BrCF_2CF_2NO/CF_2=CF_2$	1:1	2.6
17.	W.O.-64.1	$CF_3NO/CF_2=CFOCF=CF_2$	1:1	16
18.	W.O.-56.1	$CF_3NO/CF_2=CF_2/CF_2=CFOCF=CF_2$	6:5:1	5
19.	W.O.-54.2	$CF_3NO/CF_2=CFOCF=CF_2$ + ClNO	1:1 + ClNO	2
20.	W.O.-46.1	$CF_3NO/CF_2=CF_2/CF_2=CFOCF=CH_2$	3:2:1	5.5
21.	W.O.-57.1	" / " / "	6:5:1	5
22.	W.O.-68.1	" / " / "	5:4:1	7.5
23.	W.O.-17.3	" / " / "	5:4:1	260
24.	Q.C.-35.2.1	" / " / "	19:14:5	23
25.	Q.C.-35.2.2	" / " / "	19:14:5	20
26.	W.O.-51.1	" / " + CF_3OF	3:2:1 + CF_3OF	6.5

APPENDIX E (Cont'd)

POLYMER SAMPLES SUBMITTED

No.	Designation	Polymer	Charged Monomer Ratio	Amount (g.)
27.	W.O.-81.1	$CF_3NO/CF_2{=}CF_2/CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2NO$	8:9:1	25
28.	W.O.-81.2	" / " / "	16:17:1	15
29.	W.O.-80.1	$CF_3NO/CF_2{=}CF_2/CH_3O\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2NO$	17:18:1	9
30.	W.O.-80.2	" / " / "	17:18:2	20
31.	W.O.-80.3	" / " / "	17:18:1	23
32.	Q.C.-58.1	" / " / "	9:10:1	22.5
33.	Q.C.-59.1	" / " / "	4:5:1	16.4
34.	Q.C.-59.2.2	" / " / "	4:5:1	34
35.	Q.C.-59.4	" / " / "	21:25:4	165
36.	Q.C.-59.5	" / " / "	21:25:4	245
37.	Q.C.-59.6	" / " / "	24:25:1	82
38.	Q.C.-79.2	$CF_3NO/CF_2{=}CF_2/CH_3OCF{=}CF_2$	5:4:1	15.5
39.	Q.C.-79.5A	" / " / "	5:4:1	60
40.	Q.C.-79.5B	" / " / "	5:4:1	48.5
41.	Q.C.-84.1	$CF_3NO/CF_2{=}CF_2/CH_3OCFClCF_2NO$	4:5:1	19
42.	C.W.P.-6	$CF_3NO/CF_2{=}CF_2/CF_2{=}C{=}CF_2$	2:1:1	19.5

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13. ABSTRACT

This report describes work carried out in the area of nitroso polymers. Two general classes were investigated. These were (1) sulfur-containing nitroso polymers and (2) nitroso polymers containing functional groups.

Synthesis of a wide variety of fluorine-containing nitroso compounds and olefins is described, as well as the synthesis of various fluorine-containing intermediates.

Nitroso copolymers and terpolymers were prepared containing functional groups such as halogen, ester, double bonds, and methoxy. Properties of selected systems are described.

A terpolymer which could be cross-linked by peroxide was prepared using methyl 4-nitrosoperfluorobutyrate as the termonomer.

Infrared spectra and NMR analysis of the new monomers and polymers are included.

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	ROLE	WT	ROLE	WT	ROLE	WT
Synthesis (Chemistry)	8		8			
Copolymers	2					
Terpolymers	2					
Nitroso rubber	2		2			
Fluorine	1					
Sulfur	1					
Halogens	1					
Esters	1					
Physical properties	8		8			
Monomers			2			